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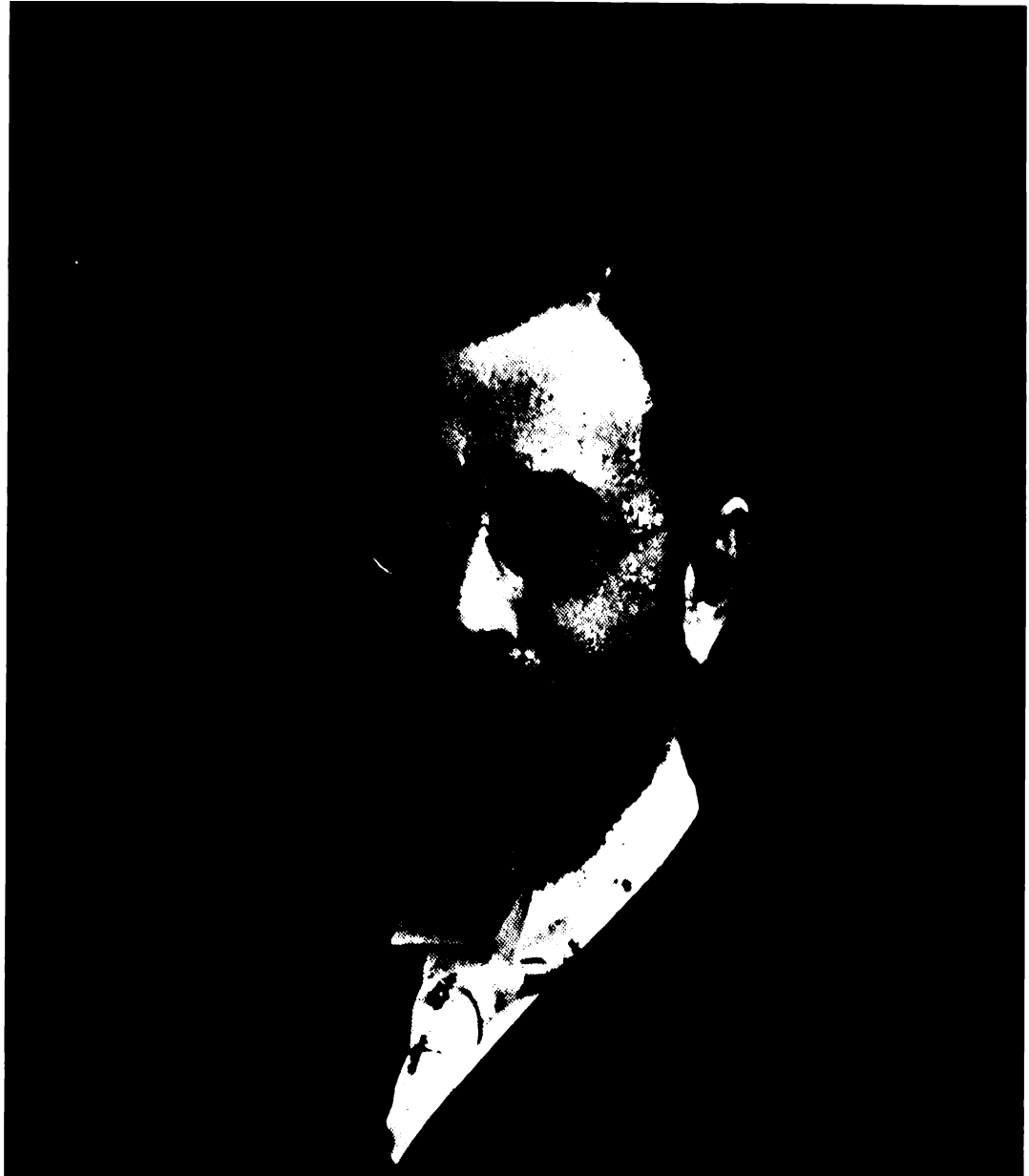

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American Electrochemical Society

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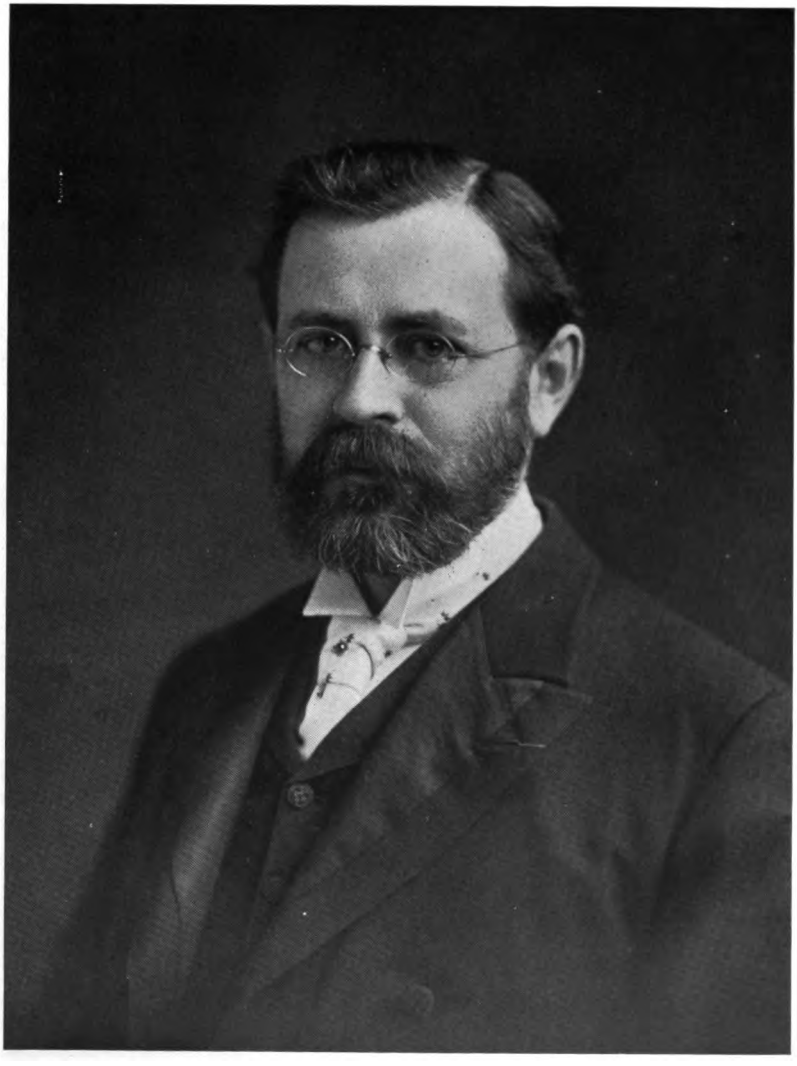

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TRANSACTIONS

OF THE

AMERICAN

ELECTROCHEMICAL SOCIETY

VOLUME [illegible]

NINTH GENERAL MEETING

ITHACA, N. Y. MAY [illegible]

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY
39 SOUTH TENTH STREET, PHILADELPHIA, PA
1906

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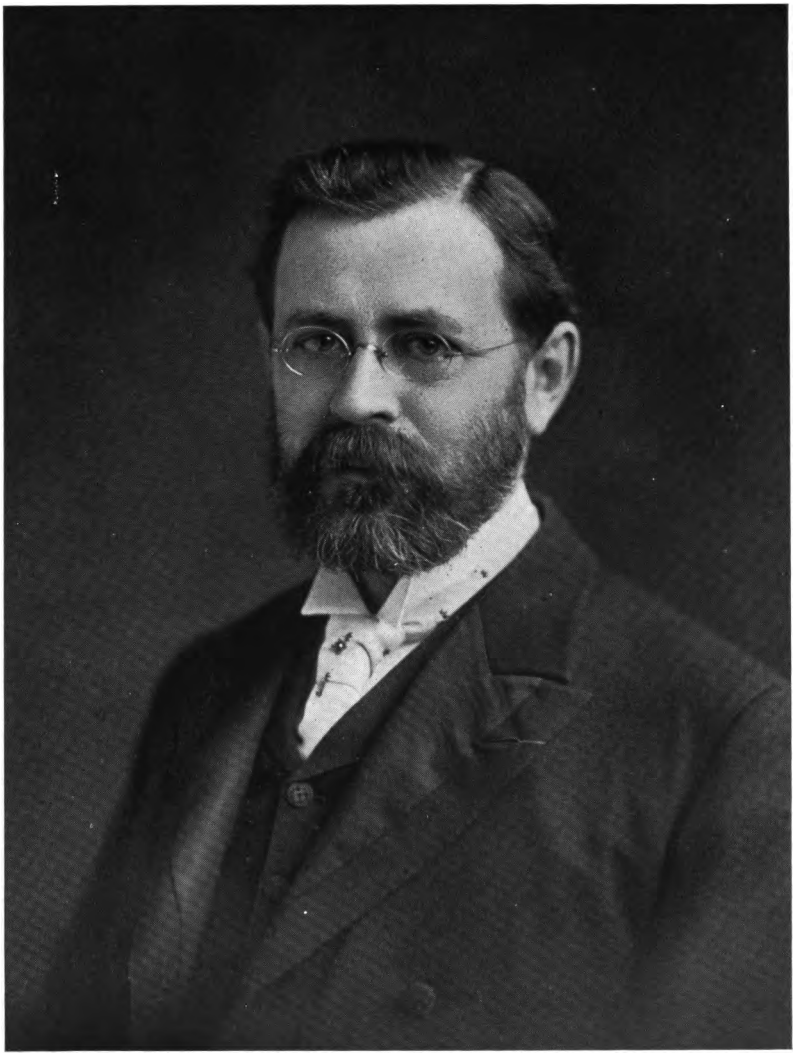

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TRANSACTIONS

OF THE

AMERICAN

ELECTROCHEMICAL SOCIETY

VOLUME IX.

NINTH GENERAL MEETING

ITHACA, N. Y., MAY 1, 2 AND 3, 1906.

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY
39 SOUTH TENTH STREET, PHILADELPHIA, PA.
1906

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VOLUME IX. 1906.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE NINTH GENERAL MEETING OF THE SOCIETY, HELD AT CORNELL UNIVERSITY, AT ITHACA, N. Y., MAY 1, 2, AND 3, 1906.

(Number of members registered, 39; guests, 33; total, 72.)

SESSION OF TUESDAY, MAY 1.

The meeting was called to order at 10 A. M., in the Chemical Lecture Room, Morse Hall, President Bancroft in the chair. The chairman of the local committee opened the meeting by introducing the President of Cornell University, as follows:

PROF. L. M. DENNIS: In opening this session of the American Electrochemical Society the University's welcome to our guests will be extended by one who needs no introduction by me—President Schurman.

DR. SCHURMAN: Mr. President and members of the American Electrochemical Society: I appreciate very much the privilege of welcoming you to Cornell University. I suppose wherever you have met in the past, those who welcomed you have pointed out some peculiar propriety in the place of meeting; and it may be difficult for us, coming at this comparatively late period in your

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history, to convince you that there is an eminent propriety in your meeting at Cornell University. Nevertheless I feel it to be the fact. The man who founded this University, a great many of the men who have supported it with their means, and a large number of the men who have constituted and to-day constitute the faculty, feel that the most important work in which a university can engage—I do not say the only work, but one of the most important works in which it can engage—is the discovery of truth with regard to nature, and the application of that truth for the comfort and convenience and improvement of man's estate.

This Society, comparatively new as it is, as I understand it, embodies this ideal. Scientists engage in the investigation of nature, the observation of phenomena, the formulation of laws, the elaboration of theories. That you hold in common with scientists in all fields of research, but in addition to that I understand it is a function of yours to apply the science which you thus discover to the improvement of man's condition; to enable man to acquire a larger mastery over nature; and that in the use of electrochemical methods you have been able to solve problems which were hitherto unapproachable or insoluble by ordinary chemical methods.

We feel, therefore, that in a way, this Society represents (what shall I say?) the most modern and the highest potency of that ideal for which this University has so conspicuously stood. I mean the ideal of scientific discovery and its application to the industrial arts. And I think that as you wander about this campus, while you certainly will not miss buildings devoted to the ancient culture, while you will not miss faculties whose main function is not the enlargement of knowledge but the cultivation of taste and the faculty of appreciation, on the other hand you will find everywhere, buildings devoted to science and you will meet everywhere men, whose primary function is teaching indeed, but who combine with their teaching scientific investigation and who, having discovered new truths, like you, wish to apply them to the arts for the benefit of mankind. I think, therefore, you will feel yourselves peculiarly at home in the atmosphere of this University, scientifically speaking. We want you to feel at home; we shall endeavor to make you feel at home; and we may in this connection announce to you that the University desires the privi-

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lege of entertaining you as its guests at luncheon during your meetings here to-day and to-morrow.

While we shall in this way and in other ways endeavor to make your visit agreeable to you, we shall expect and I am confident we shall receive a stimulus for our own scientific work, and that the men in this University who are engaged in the science or engineering or both which you represent, will feel, after you have gone, that they have received a new afflatus—an inspiration—from your visit. And though I am in the presence of these men (and perhaps in any event it is scarcely modest for me to say what I am going to say of our own institution,) we are nevertheless proud of what the men of Cornell University, who stand for your line of work, have been able to achieve for us and for their sciences.

So, gentlemen, with all my heart I welcome you to our midst; I put all we have at your disposal; I earnestly hope that your session may be a happy, prosperous and fruitful one.

PRESIDENT BANCROFT: Mr. President: If I were not a member of the teaching staff, I should dilate at some length on the pleasure that it gives us to come to Ithaca and to inspect Cornell University and its equipment. Under the circumstances, of course, it would hardly be proper for me to do that; and I shall have to differentiate my dual capacity. As President of the American Electrochemical Society I thank you heartily for the warm welcome you have given us, and as a member of the teaching staff I assure you that our colleagues and ourselves will do our best to make the visiting members enjoy their visit here and remember it as long as possible.

The following report of the tellers of election was then read:

REPORT OF TELLERS OF ELECTION.

To the American Electrochemical Society:

GENTLEMEN:—We have examined the ballots delivered to us by the Secretary, in accordance with the Constitution and By-Laws, and have the honor to report as follows:

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Legal ballots	154
Invalid	20
Unidentified	5
Total number of ballots cast	179

The ballots were as follows:

For President: Carl Hering, 111; C. F. Burgess, 21; C. J. Reed, 7; W. R. Whitney, 7; E. G. Acheson, 6.

For Vice-President: S. P. Sadtler, 119; J. W. Richards, 104; S. Reber, 93; C. O. Mailloux, 76; W. D. Bancroft, 13; E. G. Acheson, 7; C. J. Reed, 5; C. F. Burgess, 3; W. R. Whitney, 3; R. M. Thompson, 2; C. P. Townsend, 1.

For Managers: C. J. Reed, 134; E. G. Acheson, 122; C. F. Burgess, 122; S. Reber, 10; F. J. Tone, 6; A. G. Betts, 3; F. M. Becket, 2; C. O. Mailloux, 2; E. R. Taylor, 2; W. R. Whitney, 2; C. A. Doremus, 1; R. E. Fowler, 1; Carl Hering, 1; A. von Isakovics, 1; J. W. Richards, 1; T. W. Richards, 1; E. J. Roeber, 1; W. J. Taggart, 1; J. W. Walker, 1.

For Treasurer: Pedro G. Salom, 148.

For Secretary: S. S. Sadtler, 142; C. P. Townsend, 9.

Yours very respectfully,

CHARLES J. RUSSELL,
WALTER T. TAGGART,
JOSEPH W. HARRIS,
Chairman.

President Bancroft then declared the following officers elected for the various terms stated.

For President: Carl Hering, to serve for one year.

For Vice-Presidents: S. P. Sadtler, Samuel Reber, J. W. Richards, to serve for two years.

For Managers: Henry Noel Potter, E. G. Acheson, and C. F. Burgess, to serve for three years.

For Treasurer: Pedro G. Salom, to serve for one year.

For Secretary: S. S. Sadtler, to serve for one year.

The President reported that C. J. Reed had declined the elec-

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tion, and announced that the vacancy would be filled by the Board of Directors.

Papers were then read and discussed, as printed in full in the Transactions.

After the morning session, the members and guests were invited to partake of luncheon by the authorities of Cornell University, served in the lecture room, where the meeting had been held. After this, they were shown points of interest in the various chemical laboratories of Morse Hall, and the engineering laboratory, shops, dynamo room, and liquid air plant of Sibley College, practically the whole afternoon being spent in this interesting and instructive trip.

In the evening, Dr. Bancroft delivered his Presidential Address in the chemical lecture room in Morse Hall, the text of this address being given in full in these Transactions.

The members then attended a complimentary smoker, given at the Town and Gown Club, on Stewart avenue.

SESSION OF MAY 2, 1906.

The meeting was called to order at 9.30 A. M., in the chemical laboratory, Morse Hall, Cornell University, President Bancroft being in the chair.

Papers were then read and discussed, as printed in full in the Transactions.

As on the previous day, a luncheon by invitation was served in the lecture room at the close of the morning session, after which were inspected the new physical laboratory and the power plant in the Gorge, where several hundred horse-power are obtained for University purposes.

In the evening, a subscription dinner was held in the Dutch Kitchen of the Ithaca Hotel. This was one of the most successful dinners ever held by the Society, as the quaint surroundings, good attendance, and satisfaction at the already assured success of the meeting had put every one in good humor, and a very pleasant evening was the result.

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SESSION OF MAY 3, 1906.

The meeting was called to order at 9.30 A. M.

Papers were then read, as printed in full in the Transactions.

After the reading of the last paper, Dr. J. W. Richards offered the following resolution of thanks:

DR. RICHARDS: If there is no other resolution, I wish to say that this Ninth Meeting of the American Electrochemical Society has been very largely rendered a success, and interesting to all who have taken part in it, by the hospitality of the Trustees and the kind welcome which was given to us by the President of Cornell University, by the kindness of the local industries, who invited us to inspect their plants, and by the different departments of the University, who opened their halls and their buildings to our inspection; also by the hospitality of the Town and Gown Club, who opened their house for our benefit. I would therefore move you, sir, a vote of thanks to the Trustees and President of Cornell University, to the Departments of Chemistry and Mechanical and Electrical Engineering and Civil Engineering in this University; to the Remington Salt Co., and the Ithaca Gun Co., to the Board of Directors of the Town and Gown Club; and, finally, to the Local Committee, upon whose initiative and strenuous efforts have almost entirely depended the success of the meeting.

The members then dispersed to their stopping places for luncheon, after which they were met by members of the Local Committee and taken to the Remington Salt Works, on the shores of Cayuga Lake. Here, electrical energy was obtained from low pressure boilers, while the exhaust steam was used for the evaporation of the salt brines obtained from wells nearby.

This closed the official program, but the members were invited to attend a lecture by E. G. Acheson, of Niagara Falls, given to the students of Sibley College, the title of which was, "Invention and Discovery," and was as interesting to the members of the Society as to the students for whom it was designed.

In the evening, the members were invited to attend a lecture by Dr. H. W. Wiley, of Washington, D. C., on the subject of "Adulteration of Food," which was similarly a very pleasant addition to the series of interesting events that had been arranged for the visiting members of the Society.

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ANNUAL REPORT OF THE BOARD OF DIRECTORS.

To the members of the American Electrochemical Society:

We herewith submit the reports of the Secretary and the Treasurer for the year ending December 31, 1905, with some supplemental data concerning the condition of the Society since January 1, 1906.

We call attention to the supplemental statement, which shows the receipts and expenditures incurred during the fiscal year ending December 31, 1905. This shows a rather large excess of expenditures over receipts properly assignable to the past year, which, in the Secretary's report, is somewhat obscured by the actual receipts and the actual expenses during the year.

The publication of the expensive volumes which the Society sends to its members, the expense of reporting the meetings, the advance copies of papers, the issuing of the Bulletin, with the necessary cost of postage, all tend to make the expenditures high, as compared with the membership of the Society; but it is believed by the Board that the policy of holding two meetings a year, and issuing the Transactions substantially as they had been, should be kept up, even if greater economy is necessary to do this.

RECEIPTS AND EXPENDITURES CHARGEABLE TO THE YEAR 1905.

Initiation fees	$ 245 00	
Dues, 1905, paid	3,105 00	
Receipts from Transactions and advertisements,	730 26	
		$4,080 26
Expenses		$4,642 22
Deficit		561 96
Dues, 1905, unpaid		340 00

The following are the more important actions taken by the Board of Directors.

The Board of Managers, at the meeting in Bethlehem, Pa., September 18, 1905, voted to award $100 in 1906 to some member to aid him in carrying on investigations. It was then voted that the Board secure and place on file for publication in the Bulletin, a list of problems in electrochemistry, with a view of issuing the award. The proposed list of subjects were to be of assistance to the Board of Managers in making the award.

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The Board had been for some time in doubt as to what arrangements to make for the holding of General Meetings, whether there should be one meeting a year, as some members of the Society were in favor of, or two meetings, as had been customary. The following plan was, however, finally adopted. That the Society retain the spring meeting for the following reasons: The publication of the Transactions would come earlier in the year than would otherwise be possible; the attendance of members, especially those connected with colleges, would be more general, the meeting would be closer to the ending of the fiscal year, and the expense of publishing the Transactions would be better confined to the current fiscal year.

It was then agreed to hold a fall meeting each year in New York City, and to rescind the resolution concerning the abolishing of the fall meeting, passed by the Board, in Bethlehem, Pa., in September, 1905. It was believed in this way that many members would not be at additional expense for attending two meetings a year, as those who would attend the New York meeting would, in all probability, be likely to visit New York at about that time of year for other reasons. A protest against this action was filed, and the whole question will be taken up later.

Due to a request of a member, it was moved and carried that notice of situations wanted by members could be inserted free in the Bulletin up to an amount of four lines of the regular composition.

It was voted that members be asked to furnish discussions on the problems published currently in the bulletin, with a view to their ultimate publication in the Transactions.

The Frenzel Prize of $250, for the best essay on, "Practical Methods of Treating the Rare Minerals Found in America, and Extracting the Rare Metals Therefrom," was awarded to Gustave Gin, of Paris, France.

The award of $100, decided upon at the Bethlehem meeting, in September, 1905, was granted to Prof. A. T. Lincoln, of the University of Illinois, for the preparation of a research upon "Electrolytic Corrosion of Brass and Special Bronzes."

WILDER D. BANCROFT, *President.*

S. S. SADTLER, *Secretary.*

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TREASURER'S ANNUAL REPORT.

YEAR ENDING DECEMBER 31, 1905.

January 1, 1905, balance	$1,719.06
January 1st to December 31st, receipts as per list	4,205.89
	$5,924.89
January 1st to December 31st, expenditures as per list—Vouchers Nos. 14 to 60, both inclusive	4,430.48
	$1,494.47
Investment account, bought one Japanese bond	988.75
Cash balance December 31, 1905, as per bank balance	$ 505.72

PEDRO G. SALOM,
Treasurer.

SECRETARY'S ANNUAL REPORT.

FROM APRIL 25, 1905, TO MAY 1, 1906.

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN—I submit herewith the following report on the conditions of the Society:

Since the last annual report, the Society has held two meetings, and the Transactions have been published in Volumes VII and VIII.

One thousand copies of each volume, bound in cloth, and 500 of each, bound in paper, were printed.

Two hundred and fifty-four copies of Vol. VII and of Vol VIII have been distributed to members of the Faraday Society, in accordance with an arrangement for free exchange of Transactions.

There were on hand December 31, 1905:

351 copies Vol. I, cloth	228 copies Vol. V, paper.
373 copies Vol. II, cloth	254 copies Vol. VI, cloth.
255 copies Vol. III, cloth.	233 copies Vol. VI, paper.
266 copies Vol. IV, cloth	290 copies Vol. VII, cloth.
240 copies Vol. IV, paper.	244 copies Vol. VII, paper.
234 copies Vol. V, cloth.	

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And on April 30, 1906, there were on hand:

346 copies Vol.	I, cloth.	252 copies Vol.	VI, cloth.
369 copies Vol.	II, cloth.	233 copies Vol.	VI, paper.
253 copies Vol.	III, cloth.	279 copies Vol.	VII, cloth.
264 copies Vol.	IV, cloth.	244 copies Vol.	VII, paper.
240 copies Vol.	IV, paper.	415 copies Vol.	VIII, cloth.
230 copies Vol.	V, cloth.	247 copies Vol.	VIII, paper.
228 copies Vol.	V, paper.		

The following data shows the condition of the Society in regard to membership:

Total number of members, January 1, 1904	605
Total number of members, January 1, 1905	630
Total number of members, January 1, 1906	631
Number of applicants elected in 1905	57
Number of resignations during the year	24
Number of deaths	6
Number of members dropped, 1905	26

BALANCE SHEET—DECEMBER 31, 1905.

ABSTRACT OF TRIAL BALANCE.			INVEN'Y	LOSS	GAIN	ASSETS	LIAB'S	PROFIT AND LOSS ACCT.	
Cash	$510.61					$510.61			$4896.91
Profit and Loss		$4896.91							
Annual Dues		3580.00			$3580.00				
Initiation Fees		280.00			280.00				
Advertising		315.62			315.62				
Expense	2021.50			$2021.50					
Publications	4378 34		$5978.75		1595.41	5978.75			
Investments	1988.75					1988.75			
Interest		76.51			76.24				
S. S. Sadtler, Sec'y		12.50					$12.50		
Office furniture	53.00					53.00			
A. B. Frenzel Prize		250.00					250.00		
Due from Members	700.58					700.58			
Prepaid by Members		241.51					241.50		
	$9652.78	$9652.78		$2021.50	$5847 27				
BALANCE GAIN				3825.77					3825.77
						$9226.69	$504.01		
BALANCE—PRESENT PROFIT AND LOSS ACCOUNT							8722.68		$8722.68
						$9226.69	$9226.69		

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FINANCIAL STATEMENT—(JANUARY 1905, TO JANUARY, 1906).

RECEIPTS.

Cash balance, January 1, 1905	$1,723.95
From publications (Transactions)	350.88
From advertising	365.46
From initiation fees	245.00
From annual dues	3,168.31
From interest	76.24
	$5,929.84

EXPENDITURES.

For publications (Vols. VI and VII)	$2,359.14
For advertising (commission and expenses)	49.84
For secretary's salary	499.26
For stenographer's salary	328.32
For postage (office and bulletin)	348.24
For printing	845.68
For investment	988.75
Cash balance, December 31, 1905	510.61
	$5,929.84

Two volumes of Transactions, namely, Vols. VII and VIII, have been published since the last annual meeting. Vol. VII contains the papers read at the annual meeting of the Society, held in Boston, Mass., April 25, 26, and 27, 1905; Vol. VIII contains the papers read at the Eighth General Meeting of the Society, held at Bethlehem, Pa., September 18, 19, and 20, 1905.

Fifty-three papers were printed in the Transactions in 1905, as compared with forty-two in 1902, forty-five in 1903, and forty-four in 1904.

S. S. SADTLER,
Secretary.

MEMBERS ELECTED NOVEMBER, 1905, TO MAY, 1906.

November 4, 1905: Leonard Waldo, Plainfield, N. J.; W. B. Jadden, Marion, Ind.; William Smith, Phila., Pa.; C. P. Geopel, New York.

December 2, 1905: Louis Ruhl, New York; Arthur Haug, Peekskill, N. Y.; H. A. Prosser, Elizabeth, N. J.; A. Wyndham Lewin, New Orleans, La.; Francis R. Pyne, S. Bethlehem, Pa.; Harry Riley Lee, South Bethlehem, Pa.; John S. Bridges, Jr., Boston, Mass.

January 6, 1906: M. Fukuda, New York; J. H. Goodwin, Penn Yan, N. Y.; Dr. Gustav Wichern, New York; Charles S.

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Palmer, Upper Montclair, N. J.; Dr. Albert Petersson, Alby, Sweden; Washington Devereux, Phila., Pa.

February 2, 1906: E. C. Speiden, Niagara Falls, N. Y.; C. G. Schluederberg, Ithaca, N. Y.; Leon H. Buck, Niagara Falls, N. Y.; Philip P. Barton, Niagara Falls, N. Y.; R. C. Snowdon, Ithaca, N. Y.

March 3, 1906: H. J. Williams, Phila., Pa.; Henry Lacroix, Geneve, Switzerland; Samuel A. Tucker, New York; Wm. H. Nichols, LL.D., New York.

April 7, 1906: E. W. Bacon, Phila., Pa.; Jos. Lainson Wills, Brooklyn, N. Y.; E. E. Free, Ithaca, N. Y.; B. G. Klugh, Marquette, Mich.; Philip C. Walsh, Jr., Newark, N. J.

May 1, 1906: E. A. Ashcroft, New York; Arthur Hough, Dover, N. J.; Harold H. Fries, New York; A. A. Breneman, New York; Fanny R. M. Hitchcock, Phila., Pa.; A. L. J. Queneau, South Bethlehem, Pa.; Clarence M. Joyce, Arlington, N. J.; J. E. Teeple, New York; David Wesson, Montclair, N. J. George Archbold, New York; C. W. Moulton, Poughkeepsie, N. Y.; I. K. Giles, Ithaca, N. Y.; S. H. Blake, Pittsfield, Mass.; Julius Kahn, New York.

DEATHS SINCE APRIL, 1905.

Dr. Carl Kellner, elected January 8, 1903; died June 7, 1905. H. L. Williams, elected July 1, 1905; died July 4, 1905. W. B. Rankine, elected April 4, 1903; died September 30, 1905. L. Seeger, elected February 5, 1903; died March, 1905. Prof. Dr. G. Kahlbaum, elected April 3, 1902. H. S. Elworthy, elected April 3, 1902; died November 8, 1905.

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Delivered at the Ninth General Meeting of the American Electrochemical Society, held at Ithaca, N. Y., May 1, 1906, Vice-President Burgess in the Chair.

[PRESIDENTIAL ADDRESS.]

THE ELECTROCHEMISTRY OF CHEMISTRY.

By WILDER D. BANCROFT.

At St. Louis I called your attention to the manner in which a study of the chemistry involved led us to a theory of electroplating. Last autumn at Bethlehem I took up the more general question of the chemistry of electrolytic processes and pointed out how a knowledge of the chemical reactions helped us in interpreting the electrolytic reactions. To-night I am going to consider the other side of the problem and I shall try to show you that a study of electrochemistry may be of great use when we have to interpret chemical reactions.

The most striking characteristic of an electrolytic reaction is that it occurs in two places—at the anode and at the cathode. This peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes we have a chemical reaction in the ordinary sense of the word and not an electrochemical reaction. Any chemical reaction therefore which can be made to take place electrolytically must consist of an anode and a cathode process[1]. Considering the matter in this light we see that in the chemical reaction there is a possibility of the anode and cathode processes interfering, and of one perhaps masking the other.

In some cases it is easy enough to tell what the anode and the cathode processes are. If we dissolve zinc in sulphuric acid, the formation of zinc sulphate is the anode process and the evolution of hydrogen is the cathode process. Now we know that pure zinc does not dissolve readily in sulphuric acid. Consequently we should expect to find a difficulty of some sort if we electrolyze

[1] Cf. Traube, Ber. chem. Ges. Berlin, *26*, 1473 (1893); Haber, Zeit. phys. Chem., *34*, 514 (1900).

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sulphuric acid between zinc electrodes. We find this in the form of the so-called 'excess voltage' at the cathode; and in the electrolytic process we can obtain a more or less quantitative measurement of the phenomenon though we are still far from knowing the cause of it.

A less simple case is that of copper in dilute nitric acid. Copper reacts chemically with dilute nitric acid, setting free nitric oxide. The formation of copper nitrate must be the anode process and the reduction of the nitric acid the cathode process. When we start to test this we find difficulties. Everybody knows that we get ammonia instead of nitric oxide if we electrolyze dilute nitric acid, using a copper cathode. We have here an apparent contradiction, the chemical reduction yielding nitric oxide and the electrochemical one ammonia. Mr. Turrentine was good enough to solve the mystery for me. When copper reacts chemically with nitric acid, the anode product, copper nitrate, is formed at the same spot that the reduction takes place. In the electrolytic reduction of nitric acid with a copper cathode, the reduction takes place in a solution practically free from copper salt. The conditions are therefore not the same in the two cases. Mr. Turrentine therefore electrolyzed a solution of nitric acid and copper nitrate using a copper cathode. A gas was evolved at the cathode which proved on analysis to be chiefly nitric oxide. This experiment can be done in another form which is more striking. If dilute nitric acid be electrolyzed between copper electrodes, there will at first be no evolution of gas at the cathode. Gas will begin to appear as soon as the blue solution formed at the anode comes in contact with the cathode. A corollary to this is that ammonia would be formed in the chemical reaction between copper and nitric acid if the concentration of the copper salt could be kept sufficiently low. There did not seem to be any salt which one could add to the solution without introducing more complications than were eliminated. The difficulty was overcome by Mr. Turrentine in a distinctly ingenious manner. Strips of copper were hung vertically in a tall vessel. The copper nitrate flowed to the bottom of the vessel and the copper was removed by electrolytic precipitation in the form of cupric hydroxide. No current flowed through the copper strips and there was no copper cathode; but ammonia was formed.

These experiments were performed to prove that the difference

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between the electrochemical and the chemical corrosion of copper by nitric acid was an apparent one only and due to an unsuspected difference in the conditions. In addition they illustrate the superior flexibility of the electrochemical method over the chemical method. In the electrochemical method there is no difficulty in varying the concentration of the copper salt at the cathode between any desired limits, while this is very difficult to do in the case of the chemical method. This is in addition to the advantage, which the electrochemical method always has, of permitting a wide variation in the rate of reaction for constant temperature and constant concentration. If we are ever to have a thorough knowledge of the chemical reactions between nitric acid and the metals we must study the problem electrochemically.

When metals are acted on slowly by oxygen in presence of moisture, it is known that half the oxygen reacts with water to form hydrogen peroxide, this hydrogen peroxide then often reacting with the metal. By shaking a zinc amalgam with a solution containing sodium and calcium hydroxides, Traube[2] was able to isolate the insoluble calcium peroxide. So far as we now know hydrogen peroxide is formed at the anode only under special conditions, such as electrolysis of a concentrated sulphuric acid with a high anode density. Even under these conditions it is by no means certain that hydrogen peroxide is not a secondary product resulting from the decomposition of persulphuric acid. On the other hand hydrogen peroxide is the first reduction product at an oxygen cathode. In the reaction studied by Traube the oxidation of the zinc is the anode process and the formation of hydrogen peroxide is the cathode process. A consequence of this is that if we electrolyze a caustic soda solution between zinc electrodes and bubble in air round the cathode, we ought to get a corrosion at the cathode due to the secondary reaction of the hydrogen peroxide with the zinc cathode. It has been found that the cathode does corrode under these circumstances; but it is a little difficult to tell whether this corrosion is due to hydrogen peroxide or to the oxygen of the air. With an iron cathode the corrosion has never been anything like as great as was obtained by simply bubbling air against the plate when no current was passing. This

[2] Ber. Chem. Ges. Berlin, *26*, 1471 (1893).

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whole question calls for much more study than has yet been given to it.

The slow oxidation of metals in contact with solutions means the corrosion of these metals by these solutions, a very important problem. If we can substitute electrochemical methods for chemical ones, it means an enormous saving in time and a corresponding increase in the number and in the quality of the data which we can accumulate. A single experiment on chemical corrosion may easily last six weeks. This means great difficulty in keeping conditions constant. By the time that experiment has been repeated several times with the variations which each repetition suggests, six months or a year may have passed. On the other hand an experiment in electrolytic corrosion can be run through in a few hours, seven or eight at the outside. The advantage is obvious provided the results are the same in the two cases. We can see in a moment that the two phenomena must usually be the same. Suppose we have a copper plate in a sulphate solution which contains dissolved oxygen and suppose that the concentration of oxygen is not the same over the entire surface of the plate[3]. We shall then have an oxygen concentration cell with copper electrodes and a current will tend to flow through the solution from the place of lower oxygen concentration to the place of higher oxygen concentration. Since the dissolved oxygen will never be absolutely uniform in concentration, its effect will always be to start a miniature electrolytic cell. The only real difference between the chemical corrosion and the electrolytic corrosion will be in the magnitude of the current. A special case occurs when the current makes a metal anode passive. In that case the metal does not corrode in that solution. Iron becomes practically passive when made anode in caustic soda solution or in concentrated nitric acid, and iron does not rust to any appreciable extent in these solutions. An iron anode is not attacked in a carbonate solution and is attacked in a bicarbonate solution. Iron does not rust readily in the first solution and does in the second. Iron dissolves quantitatively as anode in sulphate or chloride solutions and rusts with surprising rapidity in these solutions. Nickel becomes passive in sulphate solutions and does not rust. Nickel does not become passive in sodium chloride solutions and it corrodes in these solutions, though not rapidly.

[3] Cf. Haber, Zeit. Elektrochemie, *12*, 32 (1906).

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In general we may say that any addition which makes a metal passive in any solution will prevent the metal from corroding in that solution.

You have been told to-day that electrolytic corrosion and chemical corrosion are two fundamentally different things[4]. I should prefer to word that somewhat differently and I should say that electrolytic and chemical corrosion are fundamentally one and the same. Any apparent differences will be found to be due to special differences in the conditions, as in the case of copper and nitric acid to which I have already referred. It may also happen that an insoluble salt will be formed as an adherent crust in one case and as a non-adherent powder in another. This will of course have a material effect on the rate of corrosion whether electrolytic or chemical; but such cases are perfectly simple if examined carefully. One apparent discrepancy has occurred in our own work. When pure manganese is made anode in caustic soda solution, permanganate is formed. A caustic soda solution reacts with metallic manganese chemically, forming a hydroxide of manganese and setting free hydrogen. Mr. White soon found that a manganese anode forms permanganate in caustic soda solution only when the anode current density exceeded a certain limiting value. With lower current densities manganous hydroxide or manganese dioxide is formed. The apparent discrepancy is therefore an imaginary one due to the artificial difference in the rate of corrosion.

We can now pass to the question of the corrosion of alloys, under which heading the corrosion of iron could have been taken up. Very little careful work has been done on the electrolytic corrosion of alloys and the accepted theory of the phenomena is not at all in accord with the facts. In one of the latest text-books on electrochemistry we read[5] "that obviously the potential of a mixture of two metals determines its behavior as anode." This means that the less noble metal or the less noble phase will dissolve first. In the case of copper-tin alloys annealed just above 200°, we have five possible solid phases. From 100 to 87 per cent. copper we have a series of solid solutions known as the α-crystals. From 74.5 to 67 per cent. we have the homogeneous δ-crystals, also a series of solid solutions. These are the crystals which Heycock

[4] Toch, Trans. Am. Electrochem. Soc., 9 (1906).
[5] Foerster, Elektrochemie wässeriger Lösungen, 208.

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and Neville believed to be the compound Cu_4Sn. At 61.3 per cent. copper we have the compound Cu_3Sn, the only compound in the series. From 41 to 40 per cent. we have a new series of solid solutions, the ϵ-crystals, formerly supposed to be CuSn. Lastly, we have pure tin. The experiments of Herschkowitsch[6] and unpublished work by Shepherd show that the ϵ-crystals have a potential differing from that of pure tin by only a few millivolts, while the Cu_3Sn, δ, and α-crystals differ in potential from pure copper by an even smaller amount. The order of solubility should therefore be tin, ϵ, Cu_3Sn, δ and α, the last being the least readily corroded. As a matter of fact, in most solutions tin and the α-crystals are the most readily attacked, while the ϵ-crystals are the least readily corroded.

The cause for this discrepancy between theory and experiment is that we are reasoning from static to dynamic experiments, from a stationary state to a changing one. An electromotive force is measured on open circuit with no current flowing. Electrolytic corrosion takes place on closed circuit with a current flowing.

Reasoning from electromotive force measurements to current phenomena is permissible only when no surface change takes place and when equilibrium conditions are satisfied. We know now that neither of these conditions is satisfied with the bronzes, and there is no reason for supposing that these conditions will be fulfilled except in special cases. A number of the bronzes become passive owing to the formation of a surface film of stannic oxide. In both the copper-rich bronzes and the copper-rich brasses, the reaction between the alloy and a copper sulphate solution is so very slow that no reversible equilibrium is reached during corrosion.

While we cannot predict the actual way in which an alloy will corrode, from electromotive force measurements of the phases, we can predict that any change in the current efficiency with a given alloy as anode will coincide more or less closely with the appearance or disappearance of a phase. Some experiments on the behavior of bronzes by Mr. Curry bring this point out very clearly. In sodium sulphate solutions the only phases to dissolve are pure tin and the copper-rich crystals known as the α-crystals. The current efficiency decreases as the percentage of

[6] Zeit. phys. Chem., *27*, 123 (1898).

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these two sets of crystals decrease and is practically zero for the δ, Cu_3Sn, and ϵ-crystals. In sodium acetate solutions we have a similar behavior, but the α-crystals are much less readily corroded in the sulphate solutions and the current efficiency becomes practically zero as soon as any δ-crystals are present. In sodium nitrate solutions the δ-crystals corrode until the copper content has fallen to about one-half the maximum. There is practically no corrosion with the tin-rich δ crystals, with Cu_3Sn, and with the ϵ-crystals, while alloys containing free tin corrode readily. In acidified ammonium oxalate solution, α and δ-crystals dissolve with one hundred per cent. current efficiency, while Cu_3Sn is less readily attacked and the current efficiency drops to about twenty-five per cent. Still other relations are found in alkaline sodium tartrate solutions, while with sodium chloride solutions there is no tendency for the alloys to become passive and the current efficiency is appproximately one hundred per cent. over the whole range from pure copper to pure tin.

We thus see that the electrolytic corrosion varies with the nature of the solution and that the changes in the current efficiency stand in a clearly-marked relation to the changes in the nature of the crystals present in the solid alloy. Special experiments on the chemical corrosion of the bronzes in persulphate and in chloride solutions show that the results are identical with those obtained for electrolytic corrosion in sulphate and in chloride solutions respectively. Since the identity of the chemical and the electrolytic corrosions has been proved for these two typical solutions, it is fair to assume that a corresponding identity exists in the case of other solutions. The simple relations which have been obtained in a relatively short time by a study of the electrolytic phenomena would have taken an immense amount of time if we had attempted to obtain them from a study of chemical corrosion alone. In fact it is doubtful whether any satisfactory result would have been obtained without the electrolytic corrosion. This method is obviously applicable to all other alloys and should lead to important results, especially in the case of the steels.

In this matter of corrosion we have been considering an intensely practical application of electrochemistry to chemical problems; but I should now like to call your attention to the important part which an application of electrochemistry is likely

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to play in a purely theoretical problem. In inorganic chemistry we are dealing chiefly with reversible reactions although so-called passive resistances to change are to be found in the case of potassium chlorate and also with many reactions involving gases. On the other hand, reversible reactions are the exception rather than the rule in organic chemistry. These passive resistances to change are a blessing to the organic chemist because they are what make possible the enormous number of organic compounds. On the other hand, they are a grief to the physical chemist because they interfere with his ideas on classification and because they make round-about methods of synthesis temporarily necessary. The only visible relief from these difficulties is to be found in an application of electricity. There is evidence enough now to show that most of the simpler reactions between carbon, hydrogen and oxygen are reversible when the reacting substances are exposed to the influence of the silent discharge. Thus we have the reversible reactions[7].

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$
$$CO_2 + H_2 \rightleftharpoons HCO_2H$$
$$CO + H_2 \rightleftharpoons HCHO$$
$$CO + 2H_2 \rightleftharpoons CH_3OH$$
$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$
$$CH_4 + CO \rightleftharpoons CH_3CHO$$

So far, the experiments with the silent discharge have been made chiefly to show that the reaction takes place and not with the intention of studying the equilibrium. The question however comes up whether the experiments have been made in the best possible way. Löb has shown that the equilibrium varies with the wave form of the current[8]. It is probable that the equilibrium is a function of the voltage. If this is so, it follows that an alternating current is the worst possible one to employ. With an alternating current we have every possible voltage between zero and the maximum. The equilibrium relations under these circumstances refer to a jumble of voltages and it is not surprising that conflicting results are obtained. What we need to try is the

[7] Löb, Zeit. Elektrochemie, *12*, 282 (1906).
[8] Zeit. Elektrochemie, *12*, 286 (1906).

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effect of a high-tension direct current so that we shall be working under a constant difference of potential. It may be that this will prove unsuccessful and it may be that a fluctuating voltage is essential; but there is no obvious reason why this should be the case[9] We know that the differences of potential between two levels in the air may be as much as fifty volts per meter though the average value is more nearly two volts. Berthelot states that the differences are 20-30 volts per meter in pleasant weather and may be 400-500 volts per meter in rainy weather.[10] He has also shown the importance of these potential differences in promoting the growth of vegetation. Although the sign of the potential difference is reversed at times, it seems to me that the electrical stimuli which the plants receive are largely direct current effects. It is therefore through an application of electricity in the form of the silent discharge that we shall increase our knowledge of two important chemical problems, the equilibrium relations of organic compounds and the methods of plant synthesis.

[9] Berthelot's experiments with ozone are fairly conclusive, Mécanique Chimique, *2*, 365.

[10] Berthelot, Comptes rendus, *131*, 773 (1900).

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 1, 1906 President Bancroft in the Chair.

AN INSTRUCTIVE LABORATORY EXPERIMENT IN APPLIED ELECTROCHEMISTRY.

By Wm. H. Walker.

One of the most important functions of a laboratory experiment in applied chemistry, as distinguished from an experiment in general or pure chemistry, is to enable the student to acquire an economic point of view. It may be assumed that any experiment selected for laboratory work provides for the exercise of the student's judgment in matters of scientific procedure, such, for example, as a preliminary analysis of the problem, judicious selection of the apparatus to be employed, the degree of accuracy demanded at each step, etc. But it is in this additional feature, namely, connecting the data obtained by experiment with the important economic considerations involved in the problem, that the experiment becomes an industrial one.

The choice of suitable experiments for a course in applied chemistry or electrochemistry may be aided by the consideration of a few general principles:

First—The process must adapt itself to reproduction upon a laboratory scale. This scale should be chosen as large as can be conveniently handled. While it is true that manufacturing operations very frequently develop difficulties which are not apparent when the same process is carried out in the laboratory, it is equally true that when working with eight or ten liters, the student will meet and can solve problems which do not obtain in handling a few hundred cubic centimeters.

Second—The raw materials and apparatus for the experiment must not be expensive. When a large class is to be given instruction in laboratory work upon the scale above indicated, the expense involved may be considerable, if care is not taken in this particular.

Third—The experiment should be one that admits of theoretical discussion. One of the greatest difficulties that a teacher has

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to meet is to get his students to use their knowledge of theoretical or general chemistry or physics in their laboratory work in industrial chemistry. The more completely and accurately, therefore, that the results of variations in the conditions of an experiment can be predicted before the experiment is begun, the more valuable it is. It is also desirable that these modifications or variations of conditions be involved in the plan of the experiment, in order that what may be called the "spirit of research," or thesis idea, may be introduced into the class work. That "research" should be rigorously delegated to special men in specially equipped laboratories, is a basic error which can do much harm in educational work. While valuable results can, in general, be obtained only by more highly trained men working through consecutive hours for a considerable time, yet the spirit of investigation can, and should, be introduced into a great deal more of our laboratory work. It is possible to divide the class into groups, and so plan the conditions of the experiment, that each group will contribute, by the average of their individual results, to the solution of the problem as a whole.

Fourth—And, possibly, most important of all, the experiment must admit of reasonably accurate work. Nothing is more nearly fatal to laboratory success than to choose, as experiments, such processes which cannot be held sufficiently under control to make concordant results possible, from each member of the class.

Finally—The experiment should, if possible, be given an economic setting. The relation which a given process bears in cost and efficiency to other processes for attaining the same end, may generally be discussed with profit.

A process which the author has found to meet all of these requirements, more or less perfectly, is the preparation of bleaching liquor by the electrolysis of brine without a diaphragm. The raw material is ordinary salt of known purity, and while the apparatus may take many forms, the following has been found convenient:

An Acheson graphite crucible, holding two liters, is saturated with paraffine, and made to serve as the container and also the anode. This is set in a cooling bath supplied with running water. The cathode is an inverted U (∩) shaped piece of hard rubber, upon the outside edge of which is placed a piece of copper wire,

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forming the cathode. The wires from the two limbs of the Ω are united at the top, and by these the rubber frame is suspended from a bearing, such as a bicycle hub. By means of this bearing, the cathode may be rotated and the solution continually agitated. While the current density at the anode may be changed only by varying the current or the volume of solution in the crucible, the density at the cathode may be changed at will by substituting a different wire or by soldering on a metal plate. The current of 20-25 amperes from a motor generator giving 6 volts, is led into the cell through a mercury cup in the end of the bearing supporting the cathode, and back to the generator through an ammeter. Across the cell is connected a small voltmeter. At

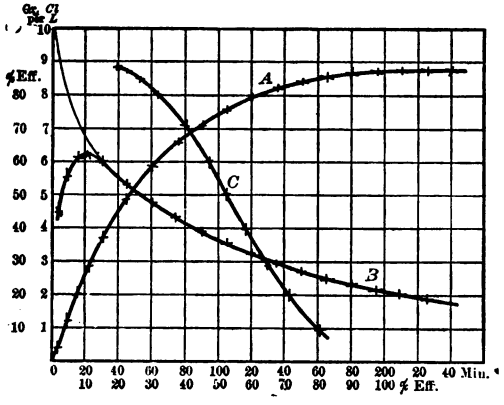

Fig. 1.

intervals of ten minutes for the first half-hour, and after that, each twenty minutes, a sample of the electrolyte is drawn from the cell by means of a 10 c.c pipette, and analyzed for available chlorine by titration with tenth-normal sodium arsenite solution. At the same time, the ammeter and the voltmeter are read and the temperature of the brine observed.

When the content of the chlorine ceases to increase appreciably, the experiment is interrupted and experimental data plotted, as shown by curves A and B in Fig. 1. As abscissae are shown, the intervals of time elapsed from the beginning of the electrolysis, as ordinates, the grains available chlorine per liter, and the average current efficiency which has been obtained

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from the start of the experiment up to the corresponding time. The calculation may be simplified and no considerable error introduced if the average of the run be taken with respect to the volume, the current strength, and the fall of potential across the cell.

In practical cotton bleaching, this liquor, however strong in available chlorine it may have originally been made, is diluted to about three grams per liter. When the available chlorine is exhausted by the cotton, the residual liquor containing the salt is discarded. It may be seen by reference to the curves in Fig. 1, that salt will be economized by continuing the electrolysis as long as any hypochlorite is being formed. On the other hand, the hypochlorite thus formed may, on account of the low efficiency

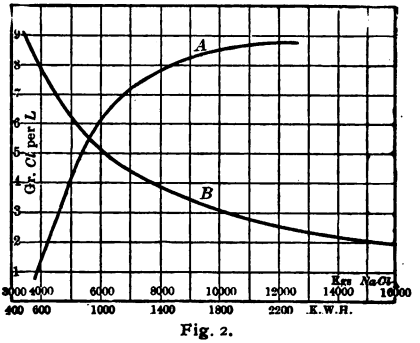

Fig. 2.

obtaining toward the end of the experiment, be costing more in power than is being saved in salt. The question then arises, for a given strength of brine, assume 200 grams NaCl per liter, and for a given quantity of available chlorine, assume 100 kg., at what concentration of hypochlorite is it most economical to stop? At what point does the cost of electricity consumed overbalance the saving made in salt consumed?

To determine the relation of the decrease in the cost of salt as the content of hypochlorite is increased, to the increase in the cost of power under the same conditions, for a given weight of hypochlorite, Fig. 2 is constructed. From the electrochemical equivalent and the average voltage across the cell, the energy in kilowatt-hours is calculated, assuming that the process was carried out at 100 per cent. efficiency. From this figure, the

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energy necessary to produce 100 kg. available chlorine, at the efficiency obtaining when the solution contained from one to ten grams available chlorine per liter is obtained, and is represented in curve A. The volume of brine, and hence the weight of salt necessary to make 100 kg. available chlorine at concentrations from one up to ten grams per liter, may be easily calculated. This is given in metric tons in curve B.

We are now in position to determine the most economical concentration of available chlorine at any particular place, if we know the cost of salt and power prevailing there. For example, assume that salt can be bought for $5 per ton, and power for 1¼ cents per kilowatt-hour. The cost of salt necessary to make 100 kg. available chlorine in the form of bleaching liquor at the ten different concentrations is given by curve A, Fig. 3. The cost of power is represented by curve B. By adding the abscissae

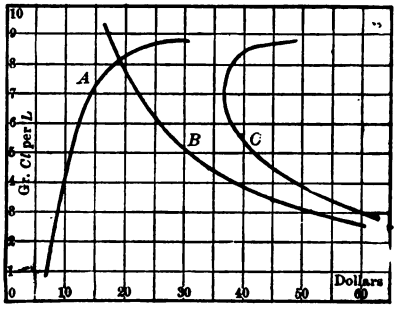

Fig. 3.

for any one concentration, we obtain the combined cost for the two factors, which is shown by curve C, with a minimum at $36.80.

In discussing the problem with the class before beginning the experiment, a number of questions will arise. For example, assuming a constant cost for salt and power, what is the most economical concentration of brine to use? From theoretical considerations, we know that the resistance, and hence the voltage necessary, will fall as the solution becomes more concentrated; this will decrease the cost of power, but increase that of salt. The reduction at the cathode will be proportionately less as the relative number of Na and Cl ions increases; this will tend to increase the current efficiency, thus decreasing the cost of power,

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while the consumption of salt is made greater. Just what this relationship is, can be determined by having a certain number of students work at each concentration of salt, from 50 grams per liter, in steps of from 50 to 350 grams.

By assembling the resultant curves in one plot on the blackboard, the results are available for the entire class.

In the same way may be discussed and made the subject of investigation by members of the class for the benefit of all, the question of the relationship of current density to the cost of the process. We can show theoretically, that to increase the size of the cathode, for example, decreases the resistance, and this lowers the energy consumed. But, on the other hand, it increases the amount of reduction of hypochlorite at the cathode, and hence decreases the current efficiency of the process, which increases the power necessary.

Such other questions as the influence of varying amounts of calcium chloride or potassium chromate upon the energy efficiency, or the influence of temperature on the resistance of the cell on the one hand, and chlorate formation on the other, may, with advantage, be taken up, if the class is large enough.

Other variations of the experiment will doubtless suggest themselves to many, but the above serve to illustrate the points which we outlined at the beginning as the desirable qualifications of an experiment in applied electrochemistry.

Mr. Warren K. Lewis, instructor in the laboratory of industrial chemistry at the Institute of Technology, has shown that the concentration of available chlorine, which corresponds to the minimum cost of power and salt, may be obtained mathematically as follows:

The curve (C) of Fig. 3, obtained by plotting the current efficiency *(e)* as abscissae, and the grams available chlorine per liter *(g)* as ordinates, may be empirically represented by a tangential equation. Choosing the point of inflection as temporary origin, any other point on the curve determines the constant, *a*, in the expression

$$x = a \tan \frac{y}{10}$$

This constant is found to be 6.82, and the equation becomes

$$x = 6.82 \tan \frac{y}{10}$$

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Transferring co-ordinates to e = 0, g = 0, we make e = x + 0.523, g = 5.0 — y, and the equation becomes

$$e = 0.523 + 0.682 \tan(0.5 - 0.1g)$$

This equation varies from the plotted curve C by less than 4 per cent. throughout its length.

Taking the cost of power and salt given above, the cost of power necessary for making 100 kg. available chlorine at 100 per cent. efficiency is $5.81, and the cost of salt for 100,000 liters of brine (1 gram available chlorine per liter) is $155.50. Hence, at any concentration, g, the cost per kg. available chlorine, is

$$c = \frac{5.81}{e} + \frac{155.5}{g}$$

To determine the point of minimum cost, put the first derivative of c with respect to g equal to zero. Substituting the above value for e and simplifying, we get

$$g \sec(.5 - .1g) = 19.8[.525 + .682 \tan(.5 - .1g)]$$

Solving this equation for (g) by approximation, we find $(g) = 7.18$ when $(e) = 38.3$, and (c) is found to be $36.86. The minimum cost, as obtained by the graphical method, is $36.80.

DISCUSSION.

DR. J. W. RICHARDS: I am very much interested in the relation of this experiment, because I have been doing some classwork myself, in very nearly the same way; that is, by dividing the class up into sections and letting them all work on the same problem, but on different parts of it; so that when the whole is compiled there are some very interesting results brought out without incurring the tedium of one man or a pair of men going over them all together. I have found it adds very much to the interest of laboratory work, however, if you can, as far as possible, give the men something new to work on; and the problem of working with sodium chloride and hypochlorite is one well established. If you can get some new product or some new process which has just been proposed and while your student is working on that get a result which cannot be found already published—that adds immeasurably to the interest of the work; and, finally, I commend

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very heartily the idea of having on a diagram dollars and cents as one of the co-ordinates. That gives point to the whole story.

PRESIDENT BANCROFT: There is another side to this which interests me as having to teach the subject; and that is, that it takes a great deal of time to work out satisfactory experiments for the laboratory course in electrochemistry; and therefore it is a great comfort to have a certain part of this work done for us by somebody else. I am very much in hopes that next year we can profit in our laboratory teaching by reason of this paper of Mr. Walker.

MR. CARL HERING: Is it not more usual in such diagrams to reverse the co-ordinates so that the minimum distance will be the vertical one, instead of the horizontal one? The graphical method that Dr. Walker described is a well-known one, and it seems to me that the more usual way is to have the quantity whose minimum you seek made the ordinate and not the abscissa.

DR. RICHARDS: The reason is essentially, I think, that we are used to consider price as being high or low, and we look for a minimum height as representing a minimum price.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 1, 1906. President Bancroft in the Chair.

SOME PRINCIPLES OF RESISTOR FURNACE DESIGN.

By Clarence Lyman Collens 2d, E. E.

In this paper an effort will be made to obtain by the aid of some of the fundamental laws of thermokinematics, a few general equations which will be of some assistance in the operation and design of electric furnaces of the resistor type. As far as possible the higher mathematics will be avoided, as it is merely the intention to show in a general way how certain varying conditions affect the thermal efficiency of a furnace, without deriving complicated equations, even though these latter would express accurately how the varying conditions are themselves interrelated.

The discussion is limited to intermittent resistor furnaces in which the net chemical reaction, if there is any, is endothermic, and relates more especially to furnaces in which the heat generating body, or resistor, is separate and distinct from the materials to be acted upon. A general knowledge of the subject is assumed.

I. General.

In the simplest type of furnace of the character described, namely the single resistor furnace, the resistor becomes the region of highest temperature from which the heat is diffused by conduction, radiation, and convection through the surrounding materials under treatment with a gradual fall in temperature throughout the mass. The surface separating the resistor and the materials under treatment may be termed the *surface of productive heat diffusion.* From this surface the heat flows outward through the furnace along lines which in general follow the paths of least resistance, or of highest thermal conductance. The different isothermals, or surfaces passing through points of equal temperature, cut the lines of flow of heat at right angles, and are usually parallel surfaces of similar outline conforming in general shape to, and surrounding, or concentric with, the resistor itself.

The heat flowing outward from the surface of productive heat

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diffusion raises the temperature of the materials adjoining the resistor and finally produces in these materials the desired reaction or effect. This must usually be carried on between definite limits of temperature, and in this discussion the minimum and maximum temperature limits of any chemical reaction or effect will in all cases be designated by θ_1 and θ_2 respectively.

It is assumed that no heat is generated in the materials surrounding the resistor, or in other words, that the flow of electricity is limited to the resistor itself. It is also assumed that the heat is diffused principally by conduction. Within the resistor the heat is supposed to be generated uniformly in all parts, although all parts are not necessarily at the same temperature. The heat generated in the central part must inherently tend to superheat that part until the necessary difference of temperature is established to cause its flow outward. Hence the very highest

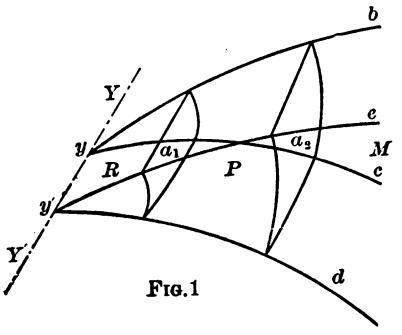

FIG. 1

temperature in the furnace is found somewhere within the resistor, and the isothermal of this highest temperature is represented by some neutral point, line, or surface along or through which there is no flow of heat, and from which emanate the lines along which all the heat generated flows outward through the furnace.

In Fig. 1 let YY' represent the neutral axis of the resistor R of an intermittent single resistor furnace of the character described above, and let a_1 represent a small section of the surface of productive heat diffusion. The area a_1 is bounded by, or enclosed within, a series of lines of flow of heat whose outer limits are yb, yc, y'd, and y'e. All of the heat generated in the

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section of the resistor between the area a_1 and the portion yy' of the neutral axis YY' will be expended in heating materials, or in performing chemical work, within the limits of the lines yb, yc, y'd, and y'e. Hence the section of the furnace bounded by these four lines and the axis YY' represents an integral part entirely independent of the rest of the furnace as far as any interchange of energy is concerned, and an investigation of what takes place in this integral part can be used in determining the action within the furnace as a whole.

When the furnace first starts up, all parts are at the same temperature θ_0 and no action takes place until the surface of productive heat diffusion a_1 reaches the temperature θ_1. Let t' be the time required for a_1 to reach this temperature. The reaction or effect desired in the adjoining materials M then commences and with a proper supply of energy in R the temperature of the area a_1 gradually rises and the isothermal surface θ_1, gradually recedes from the surface a_1, the product P being formed between the two. It is assumed that there are no other chemical reactions in the materials M below the temperature θ_1 or in the product P above the temperature θ_1.

After a definite interval of time T, usually predetermined, and generally some period of time before the surface a_1 has exceeded the temperature θ_2, the supply of energy is cut off. At this moment assume that the isothermal θ_1, or that section of it within the limits of the integral part of the furnace here considered, has reached the position and assumed the area a_2.

Of the total amount of energy supplied to this small section of the furnace during the time T, part is required to heat and superheat the resistor itself and the balance all passes into the surrounding materials through the area a_1. Of the total amount of heat passing through the area a_1, part is required to bring the materials M to the temperature θ_1, part to produce the reaction or effect itself, that is, the conversion of the materials M at the temperature θ_1 into the product P, part is necessary to superheat the product next the resistor, and part is wasted in heating the materials beyond the area a_2. This area is, in fact, the dividing line between the zones of productive and non-productive heating, as all the material inside the area a_2 is converted into product while any heating of the material beyond the area a_2

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during any stage of the run, is finally dissipated throughout the mass without productive results. This area, namely the final position and area assumed by the isothermal θ_1, may be termed the *surface of non-productive heat diffusion.*

II. Energy Consumed.

1. *In Heating and Superheating the Resistor.*

The amount of energy e_1 required to heat uniformly all parts of the resistor R to the temperature θ_1 depends upon the mass heated and the number of degrees rise in temperature; or if

v=the volume of the section considered

D_R = its weight per unit of volume

C_R = average value for the range of temperature θ_1—θ_0 of the amount of heat required to raise unit weight of R one degree in temperature;

then

$$e_1 = vD_R C_R (\theta - \theta_1) \qquad (1)$$

This merely represents the heat necessary to uniformly raise the resistor R to the temperature θ_1. Inherently, however, a difference of temperature must be established in order to maintain the flow of heat outward through a_1.

Hence when a_1 is at the temperature θ_1, the neutral axis YY′ is at some higher temperature θ^1, and there has been required some definite expenditure of energy e_2 to effect this superheating. The value of e_2 cannot readily be expressed by an equation as it depends so much upon the shape of, and energy distribution in, the resistor, but in general it increases with θ^1—θ_1, with vD_R, and with C_R; whereas θ^1—θ_1 increases in turn both as the thermal conductance of the section of the resistor between YY′ and a_1 decreases and as the rate of energy supply per unit of volume increases; and finally the thermal conductance of the section considered varies in turn with the specific thermal conductance K_R of the material R and in general with the shape of the resistor, or the ratio that the area a_1 bears to the volume v. In comparison with the other energy values here considered e_2 would be negligible.

When the difference of temperature θ^1—θ_1 has once been established in the resistor, if the amount of heat flowing through a_1 is practically constant, for every degree that a_1 is practically

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constant, for every degree that a_1 is increased in temperature, there must be a corresponding increase in temperature of every intermediate point between a_1 and YY'. Hence if K_R and C_R are constant, or represent average values for the total range in temperature in the furnace, there is required for the further superheating of the resistor an expenditure of energy

$$e_3 \; vD_R \; C_R \; (\theta'' - \theta_1) \qquad (2)$$

where θ'' represents the final temperature of a_1. The value of θ'' may be equal to or less than θ_2.

Hence neglecting e_2 we find that the total energy required to heat and superheat the resistor is represented by

$$e_1 + e_3 = vD_R \; C_R \; (\theta'' - \theta_0) \qquad (3)$$

2. In Heating the Materials M.

The amount of energy expended in heating the materials M is represented by the total amount of heat diffused from the area a_1 as it rises in temperature from θ_0 to θ_1 plus the total amount of heat diffused from the isothermal surface θ_1 as it advances from a_1 to a_2. These two values will be denoted by e_4 and e_5 respectively.

From one of the fundamental laws of thermokinematics we know that the heat flowing in unit time through each unit of area of two infinite parallel surfaces is equal to

$$\frac{K}{d} \; (v - v') \qquad (4)$$

where v and v' are the temperatures of the surfaces from and to which the heat flows, d the distance between the two, and K the thermal conductivity of the material in question.

In the section of the furnace shown in Fig. 1, take any two isothermal surfaces in the materials M outside of the isothermal θ_1 and let these two isothermal surfaces be infinitely near together or separated by the distance dx, x representing the distance from the neutral axis of the resistor measured along a line of flow of heat. Let θ and $\theta + d\theta$ be the temperatures of the isothermals corresponding with the distances x and $x + dx$ and let K_M be the thermal conductivity of the materials M. A small section of these two isothermals may evidently be treated momentarily the same as a section of two infinite parallel

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surfaces and from the law expressed above, if we consider heat positive which flows in the direction in which x increases, we find that the heat per unit of area which flows in the infinitely small period of time dt from the isothermal θ to the isothermal $\theta + d\theta$ equals

$$-K_M \frac{d\theta}{dx} dt \qquad (5)$$

The expression $\frac{d\theta}{dx}$ is recognized as denoting the rate of change of the temperature along any line of flow of heat passing through the unit area in question. If θ is a decreasing function of x, as in the case of the resistor furnace we are discussing, its differential is negative and expression (5) taken as a whole becomes positive. This point must be borne in mind in the equations below. If however θ is an increasing function of x, expression (5) remains negative in value which means that the heat will flow in the opposite direction to that in which x increases.

From the general law represented by expression (5) we easily deduce the equations:

$$e_4 = -a_1 K_M \int_{\theta_0, o}^{\theta_1, t'} \frac{d\theta}{dx} dt \qquad (6)$$

$$e_5 = -K_M \int_{a_1, t'}^{a_2, T} a \frac{d\theta}{dx} dt \qquad (7)$$

when a represents the variable area of the isothermal surface θ_1 as it advances between a_1 and a_2. This variable surface can usually be expressed as some function of x.

The total amount of heat diffused into the materials M is represented by the sum of the two integrals expressed in equations (6) and (7). Part of this heat is productive, that is, is utilized in heating materials which are converted into the product P and part is non-productive. The non-productive heating may be defined as the total amount of energy which during any period

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of the entire furnace run passes out into the materials lying beyond the final position and area assumed by the isothermal θ_1. This area has already been termed the surface of non-productive heat diffusion and the total value of the non-productive heat e_0 may be represented by the integral

$$e_0 = -a_2 K_M \int_{\theta_0,o}^{\theta_1, T} \frac{d\theta}{dx}\, dt \qquad (8)$$

The productive heating is obtained by subtracting e_0 from $e_4 + e_5$, or if we divide the value so obtained by the amount of heat necessary to raise unit weight of the materials M from θ to θ_1, we get the total weight of materials converted into product. Hence if

C_M = average value for the range in temperature θ_1—θ_0 of the amount of heat required to raise unit mass of the materials M one degree in temperature

w' = the weight of materials converted into product in the section of the furnace here considered,

we get

$$w'C_M(\theta_1-\theta_0) = -K_M \left\{ a_1 \int_{\theta_0,o}^{\theta_1,t'} \frac{d\theta}{dx}\, dt + \int_{a_1,t'}^{a_2,\ T} \alpha \frac{d\theta}{dx}\, dt - a_2 \int_{\theta_0,o}^{\theta_1,\ T} \frac{d\theta}{dx}\, dt \right\} \qquad (9)$$

If w equals the total weight of product obtained in the section of the furnace considered and p the weight of product obtained from unit weight of materials, the following relations may be obtained from equations (6), (7), and (9) as an alternative expression for the value of $e_4 + e_5$, or the total heat diffused into the materials M

$$e_4 + e_5 = \frac{w}{p} C_M (\theta_1-\theta_0) + \left(-K_M a_2 \int_{\theta_0,o}^{\theta_1,\ T} \frac{d\theta}{dx}\, dt\right) \qquad (10)$$

Equation (9) is more useful, however, in examining the temperature changes under varying conditions and the resulting effect

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upon the heat diffused. The thermal efficiency, as far as the heating of the materials M is concerned, is represented by the expression

$$\frac{e_4 + e_5 - e_0}{e_4 + e_5} \qquad (11)$$

More definite knowledge of these values and the integrals contained in the equations above, will be obtained when the term $\frac{d\theta}{dx}$ is examined under the section of this paper devoted to an investigation of the temperature changes in the furnace, but an analysis of equations (6), (7) and (8) shows that the thermal efficiency of the heating as defined by expression (11) depends primarily upon the values of a_1 and a_2.

The smaller the value of a_2, the area of non-productive heat diffusion, as compared with a_1, the area of productive heat diffusion, the better the efficiency of the heating. Hence it is desirable to make the ratio $\frac{a_1}{a_2}$ as large as possible. The efficiency approaches 100 per cent. if either a_2 or K_M approach zero, or if a_1 becomes practically infinite as compared with a_2. Obviously a_2 cannot equal zero, as we could not manufacture a finite mass of product within a surface having zero area. But the thermal conductivity can be made low, for if K_M in itself has a high value, the thermal efficiency can be increased by placing a material of very low thermal conductivity outside of the final position assumed by the isothermal θ_1. The specific thermal conductance of this other material would then be substituted for K_M in equation (8).

Any increase in the ratio $\frac{a_1}{a_2}$ simply means that the generation of heat is more thoroughly distributed throughout the materials under treatment. This naturally gives more efficient heating than in cases where a_1 is small as compared with a_2, or the generation of heat is centralized within a small area of productive heat diffusion surrounded by a large mass of materials. If the material under treatment also acts as the resistor, a_1 has practically infinite value and the heating is very efficient.

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3. In Converting the Materials M into the Product P.

When any part of the materials M is raised to the temperature θ_1, the reaction or effect desired takes place, requiring for the section of the furnace shown in Fig. 1 a total expenditure of energy represented by

$$e_6 = \frac{w}{p} H \qquad (12)$$

where H = the net heat required for the reaction or effect for each unit of weight of the materials M.

4. In Superheating the Product P.

As any product is formed, the isothermal θ_1 advances and with each advance all parts of the product already formed between the isothermal θ_1 and a_1 must inherently receive a slight increase in temperature in order to still supply the energy at the advancing isothermal surface. Hence as long as θ_1 advances there is required a continual supply of energy for the superheating of the product formed.

The advance of θ_1 is usually so slow, and the thermal conductivity of the product P is usually so much better than the materials M, that the temperature condition between θ_1 and a_1 is practically that of the state of steady flow of heat referred to under Section III of this paper.

As in the case of the resistor, it is difficult to express the value of the energy required for superheating the product, but if θ''' is the average temperature of the product P at the end of the furnace run and C_P the amount of heat required to raise unit weight of P one degree in temperature, the superheating of the product may be expressed by the equation

$$e_7 = wC_P \ (\theta''' - \theta_1) \qquad (13)$$

The average temperature required for this equation is that which would be obtained by multiplying each particle of mass of the product P by its temperature, taking the sum of these products, and then dividing this sum by the total mass. In general θ''' increases as both the thickness of the product formed and the rate of energy supply increase and decreases as the lines of flow of heat become more divergent.

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5. Summary.

By combining equations (3), (10), (12) and (13), the total energy consumed in the section of the furnace shown in Fig. 1 expressed in heat units equals

$$e = vD_R C_R (\theta''-\theta_0) + w$$

$$[\frac{1}{p}(H + C_M(\theta_1-\theta_0)) + C_P(\theta''-\theta_1)] + (-K_M a_2 \int_{\theta_0,o}^{\theta_1, T} \frac{d\theta}{dx} dt) \quad (14)$$

Hence as the action in the furnace as a whole is equal to the sum of its parts, the energy consumed in the furnace as a whole expressed in heat units equals

$$E = VD_R C_R (\theta''-\theta_0) + W$$

$$[\frac{1}{p}(H + C_M(\theta_1-\theta_0)) + C_P(\theta''-\theta_1)] + (-K_M A_2 \int_{\theta_0,o}^{\theta_1, T} \frac{d\theta}{dx} dt) \quad (15)$$

in which V = total volume of the resistor R
W = total weight of product formed
A_2 = total area of the surface of non-productive heat diffusion.

III. Rate of Temperature Change.

A mass whose different parts are at different temperatures may be in one of two conditions, namely (1) that in which the temperature of any point does not alter with the time, generally referred to as the state of steady flow of heat, and (2) that in which the temperature of each part is continually changing. In the former case the isothermal surfaces representing the different temperatures are fixed and stationary and the same amount of heat leaves any section as enters it. This is evidently not true in a resistor furnace of the type discussed above. In fact we will treat such furnaces for the purposes of this discussion as if the resistor R were enclosed within an infinite mass of the materials M and we will still further consider this assumption to be fairly correct even when the motion of the isothermal θ_1 through the materials M has become almost negligible.

This assumption merely presumes that the outer walls of the

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furnace are so far removed from the isothermal θ_1, or that the values of K_M and C_M, or either, are so high, that during the entire length of run the materials between the outer walls and the isothermal θ_1 never even approach the state of fixed temperatures and a steady flow of heat. Obviously the furnace must of necessity be designed so as to avoid the state of steady flow as otherwise all of the heat escaping from θ_1 would be radiated from the walls of the furnace, and the thermal efficiency after the fixed state was reached would be zero.

This refers to the thermal condition outside of the isothermal surface θ_1. Within this surface, entirely different conditions are to be met with, and it is desirable to have the resistor and the product as it is formed approach as near as possible to the state

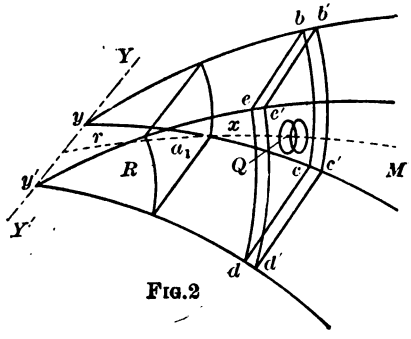

FIG. 2

of steady flow of heat so that all of the heat generated will be transferred to the zone of work.

In intermittent resistor furnaces the temperature varies with the distance away from the surface of productive heat diffusion and, if the fixed state is not reached during the entire run, it also varies with the time or length of run. We therefore have the relation, $\theta_1 = f(x, t)$. Some idea as to the nature of this function must now be obtained in order to judge of the effect of varying conditions upon the expression $\frac{d\theta}{dx}$ and consequently upon the heat diffused from any isothermal surface.

In Fig. 2 which represents the section of the same intermittent single resistor furnace as that shown in Fig. 1, let b, c, d, e, be any isothermal surface θ in the materials M, let Q be any point

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in this surface, and let x represent its distance from the neutral axis YY′ measured along the line of flow of heat passing through Q. Consider a circle having unit area drawn on the isothermal surface with Q as centre. The heat passing out through this circle in the infinitely small time dt

$$= - K_M \frac{d\theta}{dx} dt \qquad (16)$$

Now consider a second isothermal surface b'c'd'e' at the distance dx from b, c, d, e. Its temperature will be $\theta + d\theta$ and the lines of flow of heat passing through the circumference of the circle at Q will cut a second circle from the isothermal $\theta + d\theta$, whose area will be $1 + dx$, dx representing the change in each unit of area for the distance dx. The heat passing through the area $1 + dx$ in the time dt

$$= - K_M (1 + d\alpha) \frac{d(\theta + d\theta)}{dx} .dt$$

$$= - K_M \left(\frac{d\theta}{dx} + \frac{d^2\theta}{dx} + d\alpha \frac{d\theta}{dx}\right) dt \qquad (17)$$

The term $d\alpha \frac{d^2\theta}{dx}$ is omitted from equation (17), as it is negligible in comparison with the other differentials.

The difference in the heat which passes through the first circle at the isothermal θ and that which passes through the second circle at the isothermal $\theta + d\theta$ is utilized in raising the temperature of the materials between these two circles. As the expression $\frac{d\theta}{dt}$ represents the rate of increase of the temperature with respect to the time, $\frac{d\theta}{dt} dt$ will be the increase in temperature in the time dt of the small lamina between the two circles, and the heat necessary to cause this increase in temperature

$$= C_M D_M dx \frac{d\theta}{dt} dt \qquad (18)$$

since the volume between the two circles is practically equal to a cylinder dx in height and having a base whose area is unity. But the heat represented by expression (18) is equal to that represented by (16) less that represented by (17).

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Hence

$$\frac{d\theta}{dt} = \frac{K_M}{C_M D_M}\left(\frac{d^2\theta}{dx^2} + \frac{d\alpha}{dx}\cdot\frac{d\theta}{dx}\right) \qquad (19)$$
$$+ \qquad\qquad + \qquad + \quad -$$

This then is the general differential equation showing the relations which must exist between the temperature, time, and distance away from the source of heat of any point Q in the materials M. Equation (19) holds true whether we consider the materials infinite in extent or not, and is recognized as a slight modification of the well known equation for the temperature changes in the case of the motion of heat in a straight line in an infinite solid.

We know that the differential of an increasing function is positive and of a decreasing negative. In the case of the intermittent resistor furnace discussed above, θ is an increasing function of t and a decreasing function of x, whereas α is shown as an increasing function of x. Placing under the different differentials the actual signs which their values assume upon differentiation, we find that in the case cited the two terms on the right hand side of the equation tend to offset each other.

Hence speaking of actual values only we see from equation (19) that the rate of temperature change with respect to the time $\left(\frac{d\theta}{dt}\right)$ is greater the higher. the specific thermal conductance of the materials (K_M), the lower their density (D_M), the lower their capacity for heat (C_M), the greater the rate-of-change of the temperature between successive points $\left(\frac{d^2\theta}{dx^2}\right)$, and is smaller the more divergent the lines of flow of heat $\left(\frac{d\alpha}{dx}\right)$. All of these tend to increase the diffusion of the heat from a hot part to a cold part and consequently cause a more rapid change in temperature of all intermediate parts. Even the last term $\frac{d\alpha}{dx}$, measuring the divergence of the lines of flow of heat, tends to increase the heat diffusion in the direction of the line of flow as it gives a path of higher thermal conductance, but

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it also means a greater volume to be heated up in the intermediate portions and consequently a slower temperature rise.

This may be illustrated as follows: In Fig. 3 let the upper curve A represent the temperature condition in certain materials along a line of flow of heat. The materials were all at a uniform temperature to start with and it is supposed that they have been exposed to a source of heat at the point $x = o$ maintained at the temperature θ_1 for a definite interval of time t. In curve A, as also in all later temperature curves, the ordinates for the different points give the values for the difference between the final and initial temperatures, and not the values of the final temperatures of the different points. The lines of flow of heat

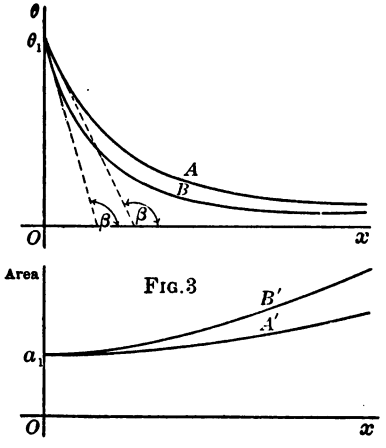

FIG. 3

are assumed to be slightly diverging and if a_1 represents a certain area on the isothermal surface at the point $x = o$, the lower curve A′ is supposed to represent the different areas which would be cut from the isothermal surfaces for different values of x by the lines of flow of heat emanating from a_1. Let the lower curve B′ represent similar areas along some other lot of lines of flow of heat emanating from an equal area a_1 at the source of heat but located at some other part of the furnace where the lines of flow of heat are more diverging.

From equation (19) we know that at the second area $\frac{d\theta}{dt}$

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will be less for any line of flow of heat included within the area. Hence every point on such a line of flow of heat will have a lower temperature value after the time t than the corresponding points in the former case and the temperature condition at the end of the time t may be represented by the curve B. No matter what the value of t this relation will always exist. But although the temperature values are less, the heat diffusion has been greater.

To prove this, consider the diffusion at the two surfaces a_1. At any instant the heat diffused from unit area of either surface is proportionate to the value of $\frac{d\theta}{dx}$. But from the discussion above we know that the temperature curve B, except at the point $x = o$ where both are maintained at the same temperature, always lags behind the temperature curve A. Hence the former must always make a greater angle with the axis o θ at the point $x = o$. Draw tangents to the two temperature curves at this point. These tangents will make some angle B with the axis ox, and the value of $\frac{d\theta}{dx}$ for each curve is equal to tanB. Hence at the point $x = o$, $\frac{d\theta}{dx}$ for curve B is always greater than $\frac{d\theta}{dx}$ for curve A, and consequently a greater amount of heat will be diffused from the surface where the lines of flow of heat are the more diverging.

An indication of the total amount of heat diffused from the surface a_1 in either case may be obtained by an analysis of the area and temperature curves. Take for instance the two curves A and A'. From curve A we get the exact temperature to which an infinitely thin lamina at any point x has been heated in the time t and from curve A' we get its volume. The product of these two multiplied by the proper thermal constants for the material in question gives the total amount of heat absorbed by this infinitely thin lamina, and the sum of such products for all values of x gives the total amount of heat diffused from the surface a_1 in the time t.

In actual practice the general shape of the isothermal surfaces after a given interval of time, can usually be determined very accurately by certain definite indications within the materials

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under treatment, such as the point where a reaction commences, or ceases, the formation or decomposition of a carbide, the point where a deposit occurs of some material vaporized in the hotter regions of the furnace, certain gradations in the color of the materials formed, etc. A white deposit may even be formed in some cases about one-fourth inch in thickness which, in cutting away the materials after a run and exposing a cross section of the furnace, gives an indication of the shape of that particular isothermal just as distinctly as if a chalk line had been drawn around the resistor. Invariably with a rectangular granular resistor the indications of the furnace show that as time elapses the isothermals gradually become rounded surfaces as shown in section in Fig. 4.

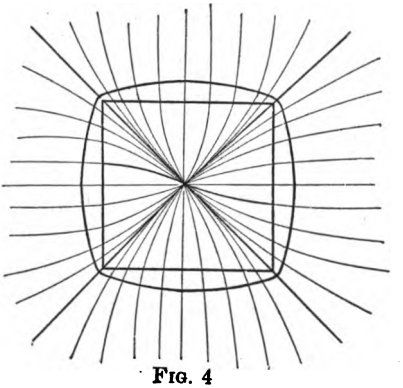

FIG. 4

This is a striking illustration of the principles discussed above as represented by equation (19). At the instant of starting, the isothermal surfaces next the resistor must have similar or rectangular cross sections, but as the lines of flow of heat at the corners are more diverging than at the sides, $\frac{d\alpha}{dx}$ is greater and consequently $\frac{d\theta}{dt}$ is less and after a definite interval of time a point a certain distance away from a corner has not increased as much in temperature as a point the same distance away from any one of the sides. This gives a lagging action at the corners to each isothermal surface as it advances outward through the

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furnace. Another way of stating this same effect is to say that there is more heat diffused from the corners due to the greater divergence of the lines of flow of heat and greater thermal conductance, and consequently the cooling action is greater.

To obtain a graphical idea of the expression $\frac{d^2\theta}{dx^2}$ in equation (19), let curve A in Fig. 5 represent as in the previous illustrations the temperature condition along any line of flow of heat after the time t, and let curve B represent a derived curve obtained from curve A, that is, the curve obtained by plotting the values

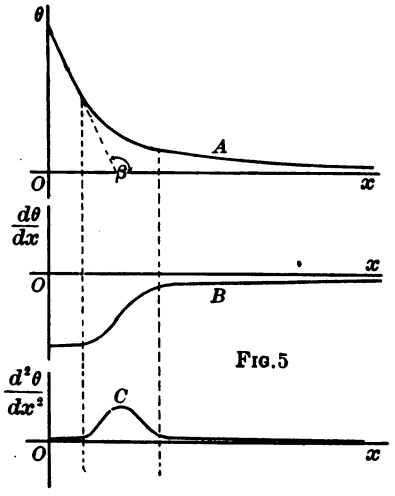

FIG. 5

of $\frac{d\theta}{dx}$, or the tangent of the angle B, for corresponding values of x. As θ is a decreasing function of x in a resistor furnace, the different values of $\frac{d\theta}{dx}$ are negative. Similarly a third curve C may be plotted which is the derived curve of the second curve B. This last curve gives the values of $\frac{d\frac{d\theta}{dx}}{dx}$, or $\frac{d^2\theta}{dx^2}$ for the condition of temperature represented by curve A. It is evident that $\frac{d^2\theta}{dx^2}$ for a given value of x is high not on account of a high value

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for θ at that point or not on account of a steep slope for the temperature curve A at the point, but solely because of a rapid *change* in the slope of the curve A at the point in question, but this same conclusion would be reached without the assistance of curves from the known significance of the expression $\frac{d^2\theta}{dx^2}$.

Hence from equation (19) we see that the more rapid the change in slope of the temperature curve at any point the more rapid the change in temperature at that point in a given interval of time. But this is almost self-evident for it simply means that the body is far removed from the state of fixed temperatures or steady flow of heat which tends to even up all irregularities in the temperature curve. As time goes on and the temperature curve tends to even up or reach a more uniform slope, $\frac{d^2\theta}{dx^2}$ and consequently $\frac{d\theta}{dt}$ become smaller and smaller, which means that the body approaches the fixed state more and more slowly and only reaches it after an infinite time.

From equation (19) we see that this state is reached when

$$\frac{d^2\theta}{dx^2} + \frac{da}{dx} \cdot \frac{d\theta}{dx} = 0 \qquad (20)$$

In the case of parallel lines of flow of heat, $\frac{da}{dx} = 0$, and the state of steady flow is reached when $\frac{d^2\theta}{dx^2} = 0$. This means that $\frac{d\theta}{dx}$ is a constant and that a curve showing the temperature drop along a line of flow of heat would be a straight line.

Thus by a proper treatment of equation (19) a general idea of the integrals contained in equations (6), (7), and (8) may be obtained. It does not serve to determine exact values for these integrals, but it shows in a general way how the value of the integrals vary with different conditions in the furnace. It also gives us an accurate idea of what would be the temperature condition in a furnace after a certain interval of time if we know what the temperature condition is at any given instant.

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As an example, let curve A in Fig. 6 represent the temperature condition in the materials of a furnace outside the resistor and let curve D be the area curve showing the divergence of the lines of flow of heat starting from unit area at the resistor. From these two curves, we derive the curves B, C, and E, representing the values of $\frac{d\theta}{dx}$, $\frac{d^2\theta}{dx^2}$, and $\frac{da}{dx}$ for corresponding values of x.

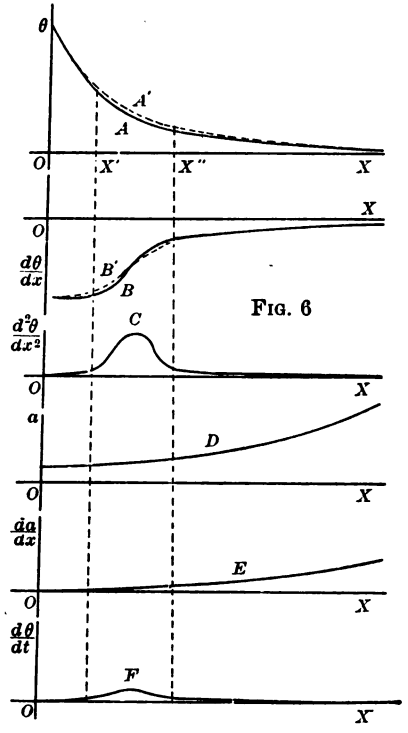

FIG. 6

These latter curves give us all of the terms contained in equation (19) and from the known value of $\frac{K_M}{C_M D_M}$ we get a sixth curve F for the value of $\frac{d\theta}{dt}$ for different values of x.

Multiplying the values of curve F by dt and then adding these products to curve A, we are able to get a general idea of the

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temperature condition after the interval of time dt. This is shown by curve A′ from which we derive the new values of $\frac{d\theta}{dx}$, as shown by curve B′. The greatest absorption of heat has evidently taken place in the zone between x′ and x″.

Hence in order to have an efficient heating of materials within a given zone of productive work, it is necessary to maintain a temperature condition, the slope of whose curve is very steep at the beginning of the zone and very flat outside of the zone of heating.

In order to obtain an accurate equation for the temperature expressed in terms of x and t, it is necessary to integrate the general differential equation (19) so as to satisfy certain other equations relating more specifically to the existing conditions. Although the equations are very complicated, this can be done if α can be expressed in terms of x. In the case of isothermal surfaces which are concentric spheres or co-axial cylinders $\frac{d\alpha}{dx} = \frac{2}{x}$, and $\frac{1}{x}$, respectively.

The special conditions to be satisfied in the case of the intermittent resistor furnace shown in Fig. 2 are as follows, if we consider the materials infinite and if r represents the distance of a_1 from the neutral axis YY′:

(1) $\theta = \theta_0$ for all values of x when $t = 0$;

(2) If we assume that the rate of increase in temperature of a is constant and equal to k during the time t′, $\theta = \theta_0 + kt$ for the value of $x = r$ from $t = 0$ to $t = t'$;

(3) From $t = t'$ to $t = T$, $\theta = \theta_1$, for values of $x = r + z$ where z is an independent variable representing the advance of the isothermal from the surface a_1. This variable z is dependent upon the rate of energy supply at the surface a_1 available for the conversion of the materials M into product P and upon the divergence of the lines of flow of heat.

For a full and complete discussion of the methods of treating and integrating differential equations of the character of (19) reference is made to Fourier's classic work, the "Analytical Theory of Heat." In general these integrals assume the form

$$\theta = A\, e \pm \frac{K}{CD} n^2 t\, f(x) \qquad (21)$$

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where A and n are constants and e is the base of the Naperian system of logarithms. Equation (21) shows that under most conditions the rise or fall of temperature with the time is a logarithmic curve.

If we take three rectangular co-ordinate axes and let one represent the distance x measured along a line of flow of heat, the second the temperature, and the third the time, the temperature condition along this line of flow of heat in the intermittent resistor furnace described in Fig. 1 may be represented by the surface shown in Fig. 7. This figure shows a uniform advance of the isothermal surface θ_1 with the time, although this condition does not necessarily exist. It also shows the condition of the materials outside of θ_1 slightly nearer the fixed state when $t = T$ than when $t = t'$.

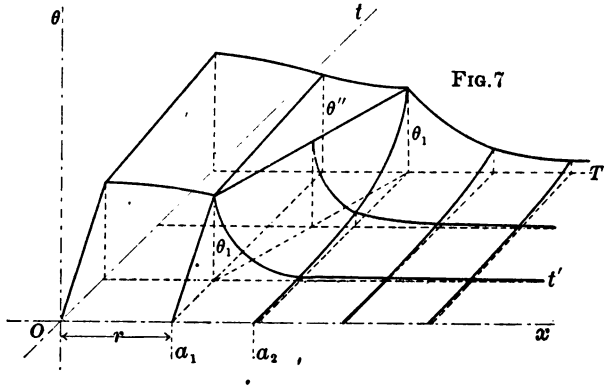

FIG. 7

A plane drawn parallel to the axes $o\theta$ and ot at any value of x cuts from the temperature surface a curve representing the increase in temperature of the point x with the time t. Similarly a plane drawn parallel to the axes $o\theta$ and ox for any value of t cuts from the surface a curve showing the temperature drop along the line of flow of heat after the time t has elapsed.

IV. Rate of Energy Supply per Unit of Surface of Productive Heat Diffusion.

In Fig. 8 let curve A represent the temperature condition at the end of the run, or after the time T, along a line of flow of heat

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in the furnace described in Fig. 1. Consider a second and similar furnace in which the rate of energy supply per unit of surface of productive heat diffusion is doubled. Neglecting for the present any consideration of the maximum temperature limit for the operation in question, the isothermal θ_1 in the second case will advance to the same position as a_2, producing the same amount of product in practically one-half the time.

It is evident, however, that the temperature condition at the end of the second run would not be represented by the same curve A for that would mean heating the materials beyond a_2 to the same temperature in one-half the time and consequently double the diffusion from the advancing isothermal θ_1. But we cannot have double the diffusion from this isothermal and still have the same value for $\frac{d\theta}{dx}$ for all values of t, which would be the case

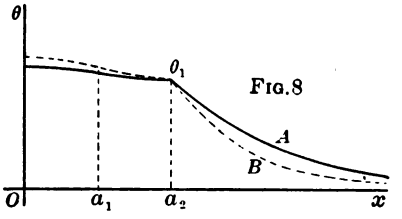

FIG. 8

if we have the same temperature curve at all stages of the run. Hence as we cannot have double the diffusion, the temperature curve at the end of the second run cannot have as high temperature values outside of the area a_2 as curve A. It assumes some lower position, represented by curve B, which, although lower in value than curve A, has a higher value for $\frac{d\theta}{dx}$ at the isothermal surface θ_1, both during the run and at the end of the run, and consequently a higher rate of heat diffusion. Thus we see that the rate of heat diffusion from the advancing isothermal θ_1 is higher in value in the second case but cannot be twice as high as that which existed in the first case. Hence we have a smaller total amount of non-productive heat diffused through the surface of non-productive heat diffusion in the second with the same weight of product formed.

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From this we reach the conclusion that the thermal efficiency as far as the heating of the materials is concerned is greater the higher the rate of energy supply per unit of surface of productive heat diffusion. A high value for the rate of energy supply and consequently a rapid advance for the isothermal surface θ_1 tends to maintain a steep slope for the temperature curve just outside the isothermal surface θ_1 with a flatter curve beyond. This condition, as has already been pointed out, gives very efficient heating in the zone between.

We must not confuse, however, this thermal efficiency with the commercial efficiency of furnaces of this type, for in actual practice a maximum economical limit is often placed upon the rate of energy supply by other items affecting the total costs. Thus if there is only a very small margin between the maximum and minimum temperature limits of a given operation, a high rate of energy supply means a very small thickness of product formed for the same total cost of loading the furnace as if the rate of energy supply had been smaller and the thickness formed greater. Or in certain cases a time element may be necessary for the reaction in question precluding too rapid rates of energy supply. But in spite of these limitations the importance of the rate of energy supply must not be minimized. In some cases the commercial efficiency may be increased twenty-five per cent. by doubling the rate of energy supply.

V. General Conclusions.

In the general discussion of the flow of heat in resistor furnaces given above, a number of assumptions have been made which are merely approximations. Furthermore certain factors affecting the thermal efficiencies have been entirely omitted. Thus it was assumed that the resistor was entirely surrounded by the materials under treatment whereas some means must be provided for conveying the current to the resistor. Consequently the very important loss of heat through the furnace terminals does not appear in the equations given. We simply know that this loss is usually greater than that which would be the case if the terminals were replaced by an equal volume of the materials under treatment.

But in spite of the assumptions and omissions, it is hoped that

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the discussion will be of some assistance in the design of resistor furnaces of the maximum possible efficiency. Some of the conclusions reached apply also to arc furnaces and to resistor furnaces in which the operation is continous instead of intermittent. The discussion can be summarized in five general principles which can usually be followed with profit.

1. Outside of the zone of productive heating, avoid, and within the zone of productive heating, endeavor to maintain, the state of steady flow of heat, or fixed temperatures.

2. Increase as far as possible the ratio that the surface of productive heat diffusion bears to the surface of non-productive heat diffusion.

3. Increase up to the economical commercial limit the rate of energy supply per unit of surface of productive heat diffusion.

4. Surround the productive zone of the furnace with materials which are as refractory as possible both as regards thermal conductivity and thermal capacity and which will still withstand the conditions to which they are exposed.

5. Avoid as far as possible in the furnace design, shapes or conditions which give outside of the zone of productive heating lines of flow of heat which are widely diverging.

The first of these five principles is the one fundamental idea of all resistor furnace design and cannot be neglected if high efficiencies are desired. The others, especially the second, third, and fourth are merely supplemental to the first and point to a few practical methods of approaching the thermal condition specified in the first principle as desirable. Thus if we have a very large surface of productive heat diffusion, and a very high rate of energy supply, a given amount of thermal work can be done in a very short interval of time during which only a very small amount of heat will be diffused into the materials beyond. This means that the materials outside of the zone of work will be far removed from the state of steady flow of heat, which is what is desired. Furthermore, a large surface of productive heat diffusion generally means that the generation of the heat is well distributed throughout the materials under treatment and that a large proportion of the entire mass is in contact with the heat-generating body. This facilitates the diffusion of heat in the productive zone and tends to maintain within that zone the state of steady flow of heat.

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Theoretically if the generation of heat is infinitely subdivided so that each particle of the mass under treatment is in contact with its particular resistor, then if the rate of energy supply is infinitely large, any reaction or effect would be produced instantaneously and simultaneously throughout the entire mass and there would be no heating of the materials beyond the zone of work.

In actual practice these principles are already being utilized to a large extent, especially the first. This is evidenced by many furnace patents. Take for instance the multiple resistor furnaces of Acheson, and furnace types in which the resistor is zigzagged through the materials from one furnace terminal to the other, as in Tone's silicon furnace or FitzGerald and Bennie's compartment furnace. In all these cases any saving effected is due to an increase in the surface of productive heat diffusion within a given surface of non-productive heat diffusion. In resistor furnaces we are principally concerned with the losses and conditions outside of

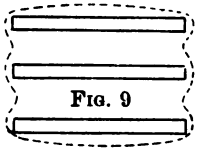

FIG. 9

the surface of non-productive heat diffusion, and there has been no assumption in the discussion above which does not make the general equations applicable to multiple resistor furnaces, or to furnaces in which the resistor is zigzagged through the materials under treatment, or in fact to resistor furnaces of almost any type where the heat diffusion is principally by conduction.

As an example of the saving effected by multiple resistors, a cross section of a three resistor furnace is shown in Fig. 9. On a certain class of work with ten inches of product formed between resistors only three or four would be formed on the top and bottom, the isothermal of θ_1 at the end of the run assuming the shape shown by the dotted line.

VI. APPLICATION OF PRINCIPLES TO SOME TYPES OF RESISTOR FURNACES.

Some of the furnaces noted below have already been discussed quite fully by FitzGerald and others, and in such cases, where

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the matter is not viewed from a new standpoint, it is merely the intention to give such supplemental information as might prove valuable.

1. Carborundum Furnace.

In his pioneer electric furnace work, Mr. Edward G. Acheson designed for the manufacture of carborundum a type of furnace having a single cylindrical resistor of granular carbon, the resistor being surrounded by the mixture of sand, coke and sawdust under treatment. A definite unit of power for the capacity of the furnace was chosen, in this case 1000 H. P. later increased to 2000 H. P. With a definite unit of power and electrical apparatus having a definite voltage range, the problem remained to determine the size or proportions of the resistor and the length of run which would give the greatest commercial efficiency. This became merely a process of elimination, different sizes being experimented with until a size was found which gave the best results.

With a cylindrical resistor the lines of flow of heat are radial, or uniformly diverging, giving an absolutely uniform diffusion of the heat from all parts, which is an important consideration in work of this character. The operation is carried on within the mixture itself, and as a mixture of sand and coke has a very low thermal conductivity nothing can be gained by the substitution of other materials outside the zone of productive work. Hence the principal factor which would enter into the determination of the most efficient size of carborundum furnace is the rate of energy supply per unit of surface of productive heat diffusion.

If the radius of the resistor is increased, its volume is increased in greater proportion than the surface of productive heat diffusion, which means that the energy required to heat the resistor itself will be greater per unit of product manufactured. With the radius of the resistor increased, the lines of flow of heat from the surface of productive heat diffusion become less diverging, which is a slight advantage but this is more than offset by the smaller rate of energy supply and consequently lower thermal efficiency. On the other hand if the radius of the resistor is decreased, the rate of energy supply per unit of surface of productive heat diffusion is increased, resulting in greater thermal efficiency. But at some point a maximum economical limit is reached. Thus if the surface

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of productive heat diffusion is halved, the rate of energy supply is doubled which means that with definite maximum and minimum temperature limits, the product can be formed to only one-half the thickness. Hence we have only one-fourth the previous amount of product formed in practically one-fourth the time, and although the smaller amount is manufactured at a higher thermal efficiency, or power cost, the labor cost of loading and unloading the furnace and other fixed charges may not have decreased in the same proportion as the output of the furnace.

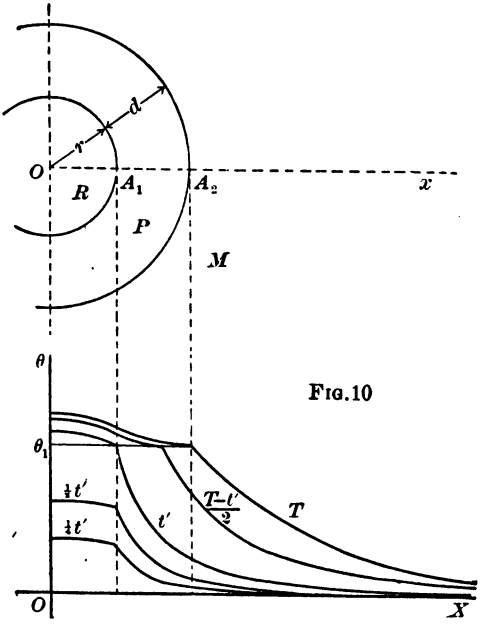

FIG. 10

Furthermore as the size of the furnace is decreased the loss in the furnace heads becomes a larger factor in the total costs. Thus we have the two extremes and by proper elimination, the economical intermediate point is determined. Even for each size of resistor, however, there is a definite length of run giving the maximum thermal efficiency, as well as one giving the maximum commercial efficiency, so that the problem is not quite as simple as it appears at first sight.

A cross section of a carborundum furnace is shown in Fig. 10

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in which the radius of the resistor is r and the thickness of the product formed d. Below this cross section is shown the temperature condition along a line of flow of heat ox at different periods of the furnace run, namely ¼ t', ½ t', t', ½ (T-t') and T, the different notations having the same significance as in the previous illustrations. As carborundum mixture is such a poor thermal conductor compared with the granular coke of the resistor, it is safe to assume (1) that during the time t' the slope of the temperature curve just outside the surface A_1 gradually becomes steeper, or in other words the rise in temperature of the resistor is more rapid than the approach of the mixture just outside the surface A_1 to the state of fixed temperatures, but (2) that after the time t' the advance of the isothermal θ_1 is so gradual that at the end of the run, the temperature condition in the mixture out-

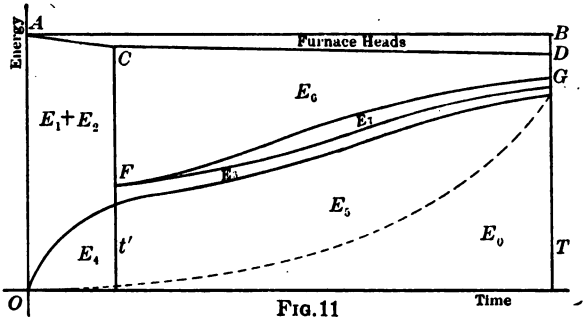

FIG. 11

side the isothermal surface θ_1 is slightly nearer the state of fixed temperatures than at the beginning of its advance. The curves shown in Fig. 10 are plotted so as to represent the assumptions just stated, which are borne out by indications given in actual furnace runs.

With the help of these temperature curves we can plot in a general way the energy consumption in a carborundum furnace, using the equations discussed under Section II of this paper. This is shown in Fig. 11, E_1, E_2, E_3, etc., representing total values for the entire furnace corresponding to the partial values e_1, e_2, e_3, etc., used in the case of an integral section of a furnace.

The energy supplied to a carborundum furnace is kept constant during the entire run and in Fig. 11 is represented by the line AB.

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During the interval of time t' all of this energy is consumed in heating the resistor ($E_1 + E_2$) and to a certain extent (E_4) in heating the mixture by diffusion through the surface A_1, Fig. 10 This latter item increases in value with the time as during the interval of time t', $\frac{d\theta}{dx}$ at the surface A_1 is continually increasing in value as shown by the temperature curves in Fig. 10. After the time t', the heat (E_5) diffused from the advancing isothermal θ_1, increases in *total* value with the time as the area of this isothermal surface increases, but it does not increase in proportion to the increase in area as $\frac{d\theta}{dx}$ decreases with the advance of the surface θ_1. The further heating of the resistor E_3 also decreases as the run progresses for the reason that the surface A_1 does not increase as rapidly in temperature towards the end of the run as at the beginning. Similarly E_7 does not increase as rapidly in value towards the end of the run. The reason for this in both cases is two-fold: (1) It is evident that the amount of energy available for the chemical reaction is gradually decreasing causing a slowing up in the advance of θ_1; and (2) even if the amount of energy available for the chemical reaction had been kept constant, the rate of advance of θ_1 would still have decreased for with its increase in area it requires a lesser thickness, or advance, to maintain a constant volume of product manufactured in unit time.

The loss of energy in the furnace terminals and the heat diffused through the terminals, if these two items are taken into account, may be represented by the area between the lines AB and ACD.

The remainder of the energy supplied to the furnace is that which becomes available for the chemical reaction and is shown on the energy chart as E_6. This has a gradually decreasing value as the run progresses, showing that the efficiency of the furnace is very much less at the end of the run than when the formation of carborundum first commenced. In fact with the length of run increased beyond that shown, the efficiency of the furnace gradually approaches zero as the lines CD and FG converge. When these two lines meet there is no more carborundum formed, the isothermal θ_1 no longer advances, and all the energy supplied to the furnace is being diffused from the surface of non-productive heat diffusion and through the furnace terminals.

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That part of $E_4 + E_5$ which represents non-productive heating in the mixture may be represented by the area E_0 below the dotted line. The form assumed by this dotted line may be obtained from the temperature curves shown in Fig. 10, which gives us a general idea of the value of $\frac{d\theta}{dx}$ at the area of non-productive heat diffusion A_2 during different stages of the furnace run. The value of $\frac{d\theta}{dx}$ at this surface increases slowly at the beginning of the run and then more rapidly as the isothermal θ_1 approaches its final position A_2.

A comparison of the two areas $E_1 + E_2$ and E_0 shows the two factors which determine the most efficient length of run for a resistor of a definite size giving a definite rate of energy supply. One of these is independent of the length of the run and the other is not. If the run is short the energy required to heat the resistor per unit of product formed is large, whereas if the run is prolonged the same may be said of the non-productive heating. Neglecting the other smaller losses, the length of run giving the highest thermal efficiency is unquestionably that which makes the areas $E_1 + E_2$ and E_0 equal. But this is not necessarily the length of run giving the greatest commercial efficiency for certain fixed charges and labor costs may make desirable a longer run with a greater amount of product formed.

So far we have merely considered the energy necessary for the heating of the mixture and the formation of carborundum. If other intermediate compounds are formed, the heat absorbed in the formation of these intermediate products would tend to still further retard the approach of the materials outside the isothermal θ_1 to the state of fixed temperatures, giving steeper temperature curves, but the discussion as a whole and the conclusions reached would not be seriously affected.

2. Siloxicon Furnace.

In his siloxicon patents, Mr. Acheson describes a furnace in which two or more resistors are used in parallel. These, as in the case of the carborundum furnace, are made of granular carbon and are surrounded by a similar mixture of sand and coke of slightly different proportions. When such a furnace first starts

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up, there is an isothermal surface θ_1 surrounding and advancing from each resistor, but at the end of the run, if the resistors are properly spaced, these surfaces combine forming one isothermal surface θ_1 enveloping all the resistors. This single surface is the surface of non-productive heat diffusion and its area bears a much smaller proportion to the combined surfaces of productive heat diffusion of all the resistors than in the case of a single resistor furnace. This means a higher thermal efficiency, other things being equal. But in the siloxicon furnace, a very low rate of energy supply is used which is one of the reasons for the selection of multiple resistors. This low rate is made necessary on account of the narrow temperature limits of the reaction. It is very probable that the low rate of energy supply more than offsets the high ratio that the surface of productive heat diffusion bears to the surface of non-productive heat diffusion and that consequently the manufacture of siloxicon is carried on at a lower thermal efficiency than the manufacture of carborundum although the single resistor carborundum furnace is not in itself an efficient type of furnace.

3. Graphite Furnace.

FitzGerald has already pointed out that in the Acheson graphite furnace the surface surrounding the crushed coal should be made as small as possible for the volume of coal which it envelops. This is the surface of non-productive heat diffusion. The surface of productive heat diffusion may be taken as the surfaces of contact between the individual particles of coal, and is infinitely large as compared with the surface of non-productive heat diffusion. As the only maximum temperature limit, if any, is that at which carbon vaporizes, a very high rate of energy supply may be used. Furthermore the surface of non-productive heat diffusion may be surrounded by the most refractory materials which it is possible to obtain. Hence on account of physical properties of the material itself, very much higher thermal efficiencies are possible in the manufacture of graphite than in the manufacture of carborundum.

4. Graphitizing Electrodes.

In the Acheson process, the carbon electrodes are arranged in rows or tiers, the length of the electrode being placed at right

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angles to the direction in which the current flows. The tiers are separated by thin sections filled with the granular resistor carbon. Although this arrangement was chosen primarily so as to allow of the treatment of large masses of electrode material in a single furnace without excessive currents or exceedingly low voltages, it is one of high thermal efficiency. As in the case of the graphite furnace, the surface of non-productive heat diffusion surrounds the mass of electrodes and should be made as small as possible for the volume contained therein. It can be surrounded by very refractory materials. The surface of productive heat diffusion is evidently the sum of the areas of the faces of the zones of heating between the tiers of electrodes and is very large as compared with the surface of non-productive heat diffusion. Hence as the limit to the rate of energy supply is the same as that in the case of the graphite furnace, very high thermal efficiencies are possible.

In the Castner process for graphitizing carbon electrodes, the current is passed lengthwise through a single electrode connected to the two furnace terminals. Theoretically such a method is more efficient thermally than the Acheson process. The surface of productive heat diffusion is infinite, being the surface of the molecules and the rate of energy supply can be made exceedingly high. But commercially the Castner process cannot compete with the Acheson process, as the labor costs are much higher. Furthermore the loss of heat through the furnace terminals in the Castner process is excessive. These must inherently be very much larger in cross-section than the carbon under treatment and are made of material which is a good thermal conductor.

5. Baking and Polymerizing Electrodes.

The Acheson process for polymerizing carbons is thermally the same in principle and design as the graphitizing process and is as efficient. In Hall's process for baking carbon electrodes the articles are placed at one side of a granular carbon resistor and are separated therefrom by a definite thickness of a material which is a poor thermal conductor. The articles are also embedded in similar materials. Obviously such a process cannot be as efficient thermally as the Acheson process.

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DISCUSSION.

PRESIDENT BANCROFT: Mr. Acheson once said that the packing of the core of a carborundum furnace was a fine art; and I think now we see, perhaps why it should be so. Another thing that occurred to me during the reading of Mr. Collens' paper is, that there is a criticism very often made about university work that we deal too much with abstract problems and integral signs. It appears, however, that the people who do things with resistance furnaces make a good deal more use of integral signs than those of us who merely play with such furnaces.

DR. J. W. RICHARDS: I had the opportunity of reading over Mr. Collens' paper before the meeting and was very much impressed by the systematic and the very capable way in which he had handled the subject, and especially impressed by the proof which he gave that the circular type of furnace with an interior resistor was in many respects one of the poorest and least efficient types of electric furnace for the producing of material, for instance, like carborundum. I think the paper is exceedingly important and has thrown light upon different kinds of electric furnace design which will be of the highest practical value.

PROF. C. F. BURGESS: I agree with Dr. Richards. Like the paper of Dr. Walker, this paper is of especial interest to us who have to deal with instructional work along electrochemical and electrothermal lines. The analysis that he has given, seems an excellent one. In discussing matters of this sort with our students it is desirable to point out in what ways practical working departs from ideal conditions; and there are certain questions upon which I should like to have further information. One of them is, whether in a technical furnace, say with the circular resistor, you get a symmetrical surface of heat realization; that is, whether the resistor is concentric with the actual distribution of heat. Another is, how large a part do the terminals play in departure from ideal conditions, and what other factors are there which come in in practical working and which are not included in this mathematical reasoning as just given to us.

MR. C. L. COLLENS: In reference to Prof. Burgess' question as to whether the isothermal surfaces are always concentric cylinders, if the resistor is cylindrical,—that is generally found to be

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the case. Prof. Burgess refers, possibly, to the influence that the vapors in the furnace have on the diffusion of the heat, or in other words, whether the diffusion of heat by convection is negligible as compared with the diffusion of heat by conduction. If all the vapors set free in the furnace ascended, they would carry up a certain amount of heat and would tend to distort the isothermal surfaces, that is, they would tend to make the isothermal surfaces bulge upwards towards the top of the furnace, due to the diffusion of heat by convection. But in all the practical work with which I have had experience the vapors seem to be diffused from the zone of work uniformly in all directions. They are forced out under such high pressure that the tendency of the vapors to rise is negligible. The pressure is uniform in all directions and the vapors are consequently forced out through the materials surrounding the zone of work along lines which in the case of a cylindrical resistor are practically coincident with the lines of flow of heat by conduction. As the vapors approach the outer walls of the furnace and meet less resistance, they tend to rise upwards, but at the zone of work in the center of the furnace, there is apparently no distortion of the isothermal surfaces due to the diffusion of heat by convection.

In resistor furnaces having open ventilated bottoms, there is always a large amount of vapor escaping from the bottom of the furnace, even through a bed of twelve or fourteen inches of tightly packed finely ground materials. In some furnaces we find, if anything, more product formed below the resistor than above the resistor. This means that the isothermal surfaces bulge downwards, which is due to the fact that in practice the bottom of the furnace usually has the best heat insulation, giving less radiation or diffusion of heat from the bottom than from the walls or top of the furnace. If in any given furnace there is any distortion of the isothermal surfaces, it can generally be attributed to irregularities in the thermal conductance of the materials surrounding the resistor and is very seldom due to the diffusion of heat by convection.

In regard to the terminals of a resistor furnace, I can give no definite figures as to the actual value of the terminal losses as compared with the total losses. I simply know that in shortening up the length of a furnace, the losses in the terminals and the

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radiation and diffusion from the terminals gradually become a much greater factor until a point is finally reached where the furnace cannot be further shortened without a loss of thermal efficiency. When a furnace is shortened up, if we keep the same cross section and if we do not decrease the total amount of energy supplied to the furnace, we must necessarily increase the rate of energy supply, and doing this should give an increase in thermal efficiency, but sooner or later we reach a limit due to the affect of the terminal losses upon the thermal efficiency of the furnace as a whole.

Regarding the factors not included in the analytical treatment, there is first the question of terminal losses just mentioned. I have also assumed that there is but one reaction taking place in the furnace, namely, that at the advancing isothermal surface θ_1. In practical work there are generally other reactions. In some cases we have secondary products formed outside of the advancing isothermal surface θ_1, and the energy required for these is not included in the discussion, although the thermal relations and conditions at any isothermal surface where a secondary product is formed, could very easily be treated analytically in the same manner as the general discussion above. If there are products formed outside of the advancing isothermal surface θ_1 which consume energy, they tend to give a steeper temperature curve outside of the isothermal surface θ_1 as the consumption of energy to form these secondary products retards the temperature rise of any given point with the time. But a steeper temperature curve outside of θ_1 means a greater diffusion of heat from the surface θ_1. Hence where secondary products are formed which consume energy, the main product is manufactured at a lower thermal efficiency than if no other products had been formed.

Products may also be formed, or reactions take place, inside of the advancing isothermal surface θ_1, such as the decomposition or vaporization of the product, or of the impurities in the product, all of which would influence the final result. Another factor not taken into account is any leakage of current outside of the resistor either through the product or through the materials surrounding the product.

But in spite of the influence of these factors, I cannot lay too

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much emphasis on the statement that their omission does not seriously affect the theoretical discussion, and does not in any way alter the conclusions reached. These latter are all confirmed by practical work upon a large scale.

MR. CARL HERING: I hope Mr. Collens or some one else will supplement this very interesting theoretical research with some actual constants accompanied by actual dimensions, so that we will have something concrete to use in the design of furnaces. The researches of Mr. Collens give us only relative figures, but not absolute ones; any one who has a furnace to design, must have concrete figures, even though they are only crude and approximate. In many of these resistance furnaces, the insulating refractory material around the resistor may become conductive when hot and may therefore carry some of the current. In that case the conditions forming the basis of Mr. Collens' researches are altered somewhat; because the resistor itself then becomes larger in diameter.

MR. COLLENS: In reference to the flow of electricity through the product, that does not in any way alter the thermal conditions outside of the advancing isothermal surface θ_1. If anything, it tends to make the operation as a whole more efficient, because less heat is required to superheat the product and the resistor. The heat is generated nearer the advancing isothermal surface and this assists in maintaining the condition of fixed temperatures inside of that surface.

PRESIDENT BANCROFT: Our experience with toy carborundum furnaces has been, that when we have a successful run we get a very pretty circle of siloxicon—showing that the isothermals are very nearly circular. Of course, when we fuse the bricks of the furnace, the result is more picturesque but it is not anything like so symmetrical.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 1, 1906. President Bancroft in the Chair.

THE ELECTROLYTE DENSITY IN STORAGE BATTERIES.

By Lamar Lyndon.

From the reversible chemical equation of the lead-sulphuric acid and lead accumulator,

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O,$$

it is obvious that, on discharge, S and O are abstracted from the electrolyte and combine with the active material of the electrodes, and the water in the H_2SO_4, thus decomposed, is released. The density and quantity of the electrolyte are therefore decreased as discharge proceeds, and, conversely, they increase with charge. This abstraction of O and S follows, exactly, the chemical formula, is proportional to the ampere hours of discharge of the cell, and independent of the rate at which discharge takes place.

Numerous experiments made in this country and abroad, particularly in Germany, seemed to indicate that the higher the rate of discharge, the less is the abstraction of S and O, and the smaller the diminution in density. Also, with a given rate of discharge, the change in density is less toward the end of discharge than in the beginning. While it was difficult to reconcile these experimental facts with the rational and basic formula, the ill-matched pair continued to go in double harness for a considerable period. Sometime in the year 1902, it occurred to the writer that an explanation of the divergence of fact and theory could be found in the retarded diffusion of the electrolyte, when the surface layer of active material has become partially sulphated and thereby closed the pores in the surface of the plate.

This condition prevents that portion of the electrolyte absorbed and contained within the pores of the active material from diffusing and mixing with the free electrolyte in the cell, nor can the free electrolyte pass into the pores of the plate and come

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in contact with the unused portion of the active material. As further discharge takes place, the only S and O available for the necessary chemical combination, is that in the electrolyte contained within the pores of the active material, and this quantity is, of course, comparatively small. The final result is, the extreme dilution of the electrolyte within the pores of the plate, while the external electrolyte is changed but little. When discharge is rapid, the surface of the plates very soon passes into the form of lead sulphate, and the increase in its volume closes up the outer pores, masking the active material and imprisoning some electrolyte within the pores of the plate, while the main body of the electrolyte in the cell is excluded from the unsulphated active material. The same condition exists when the plate has been discharged for some time at moderate rates.

From these premises, the natural conclusion was, that at the end of discharge there exist two separate bodies of electrolyte; one contained in the pores of the plates, greatly diluted—almost to the point of pure water—while outside the surface of the plates there is another body which has suffered comparatively little change. If these two bodies could diffuse and mix thoroughly, the density of the resulting mixture should be the same for a given ampere hour, regardless of the rate at which this discharge took place.

Some experiments were made to determine the correctness of this theory, which consisted in discharging a given cell at various rates and then allowing it to stand discharged for several hours. The density of the electrolyte would gradually fall, and, in every instance, approached nearly to the calculated value. The time of standing required to attain a constant value for the electrolyte density was less with a cell made up of Planté plates, having a thin layer of active material, than with a pasted plate having a thick layer, just as would have been expected. From the results of these experiments, the writer feels justified in stating that the amount of S and O abstracted for a given ampere hour discharge is constant and independent of rate or portion of the discharge. This shows the dependence of the chemical action on the electrolyte imprisoned in the pores of the active material in rapid and prolonged discharge.

The voltage decreases and the discharge ceases, not because the

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active material is used up, but because that portion of the electrolyte which is really useful has been deprived of those elements necessary to continue the chemical action. Further discharge brings the surface layer of active material again into play, because it is the only portion in contact with electrolyte containing the elements required for the production of electrical energy, and this results in an excessive sulphating of this portion of the active material. This means excessive clogging of the surface pores and increase in volume, causing flaking and consequent dislodging of active material, buckling of plates, and reduction in capacity.

From these considerations it is clear that a plate, on which the active material is thin and porous, can be worked better with electrolyte of lower density, than can one which has a thick layer. Also in cells which are subjected to rapid discharge, the electrolyte density should be greater than in cells which are slowly and moderately discharged. The required density is therefore, in a measure, independent of the total quantity of electrolyte in cells having thick plates and subjected to rapid discharge, the active quantity being partly fixed by the amount of absorption in the pores of the plate. Of course, this statement is modified by the assumption that the total quantity of electrolyte in the cell at the beginning of discharge is sufficient to maintain a reasonably high density over that portion of the discharge, in which the whole body of the electrolyte takes part, and also to provide for the diffusion which takes place slowly during discharge.

These considerations would lead to the conclusion that high density of electrolyte is advantageous, and should be generally adopted. Another apparent reason for the use of high density electrolyte is the increase in the electromotive force of a cell with increase in acid concentration. This is quite appreciable, and is a linear function of the density as shown by Streintz's formula for the electromotive force .

$$E = 1.850 + 0.00057g,$$

in which g equals grams of acid per litre of electrolyte. Thus the electromotive force of an open-cicuited cell having an electrolyte density of 10 per cent., is 1.98 volts, while with 35

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per cent. electrolyte, the E. M. F. is 2.14 volts—an increase of 8 per cent. in the E. M. F.

There are, however, other important factors which greatly modify these deductions and which fix the proper electrolyte density between 1.200 and 1.300 sp. gr., *i. e.*, between 27 per cent. and 39 per cent. of H_2SO_4.

Earle,[1] in a series of experiments on the influence of electrolyte density on the capacity of cells, tested two plates of two different thicknesses. Long previous to this work, Heim made a number of tests on the variation in capacity with different electrolyte densities. The results are shown in Fig. 1.

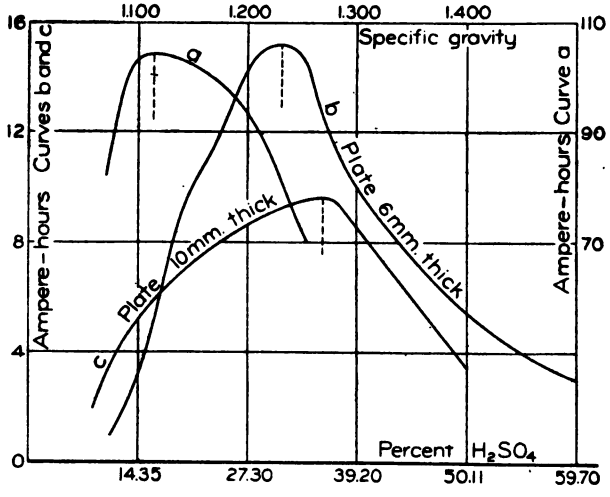

Fig. 1.

Curve *a* shows the curve of variation of capacity as determined by Heim.

Curve *b* shows variation for a plate 6 mm. thick, as found by Earle.

Curve *c* shows variation for a plate 10 mm. thick.

The maximum capacity for curve *a* is between 15 and 19 per cent., concentration.

Maximum for *b* is at about 30 per cent. concentration, and for *c*, at about 36 per cent. concentration.

[1] Zeitschrift für Electrochemie, *II*, 559 (1895-96).

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Naturally, the thicker plate requires a denser electrolyte, as is shown by *b* and *c*.

The falling off of capacity with increase in electrolyte density is puzzling, in view of the facts before given. It is explained by Dolezalek[2] as follows:

"At the beginning of the discharge, the lines of current first enter principally the outer layers of the active mass, where they find the least resistance. In the same measure as the concentration, polarization develops at the outer layers, the current lines penetrate deeper and deeper into the electrode and in such density that everywhere in the pores, the loss of potential (I. R.) is equal to the polarization prevailing in the outer layers. This condition must necessarily be fulfilled, since the active mass (lead as well as lead peroxide) is a first-class conductor, and therefore must have the same potential within the pores as without. If the polarization at the outer layers has reached the value of 0.2 volt, the potential of the accumulator has fallen at the same time by 0.2 volt, and the discharge is interrupted. At this moment the lines of current have penetrated so far into the active mass that the loss of potential in the pores (that means the product of current strength and pore resistance = I. R.), has likewise reached the value of 0.2 volt. Now the resistance of the pores is determined by the conductivity of the sulphuric acid filling them; the product I. R., herewith, will reach the value 0.2 later, giving a greater capacity; the better conducting acid is that which fills the pores.

"As is well known, the conductivity of sulphuric acid at first increases with concentration, attains a maximum at 30 per cent. H_2SO_4 (density 1.224), and then decreases again. According to the above discussion, then, the capacity must reach a maximum at a density of 1.224, as the above measurements splendidly confirm."

This, while in itself true, is misleading if not modified by the considerations as to reduction of density in the electrolyte imprisoned in the pores. Obviously, the internal electrolyte does not remain at the concentration for minimum resistance as discharge proceeds, unless the diffusion be perfect.

With thin layers of active material and low discharge rates,

[2] Theory of the Lead Accumulator, p. 168, et. seq.

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this reasoning may hold, but not otherwise. The curves in Fig. 1 show a wide variation in the acid density, which produces the maximum capacity. The whole question is simply one of rate of diffusion, and this varies with the depth and porosity of the active material and the rate of discharge. It seems strange that so distinguished an investigator should have neglected this self-evident fact. As a rule, the higher the discharge rate and the thicker the layer of active material, the higher must be the acid density for maximum capacity and efficiency. The proper theoretical density for any cell is that which will most nearly average 1.224 throughout its range of variation in concentration within the pores, and manifestly, each particular make of cell has its own best density for a given duty, determinable only by experiment.

The factors of durability and length of time between successive charges, enter into the problem, and their effect is to keep the density below certain limits. As is well known in the art, high densities greatly shorten the life of the cell, due to the rapid increase in local action and internal discharge. Cells which are required to work for several weeks on each charge, such as signal batteries, gas engine sparkers, and those for supplying power to kinetoscopes, musical instruments, and the like, would lose their stored energy by internal discharge in a short time, if the densities were too high, and would become ruined from over-sulphating.

Internal discharge means loss of energy and reduced efficiency, so that the power station batteries are also worked in low density acid.

Motor car batteries usually have thick layers of active material, and discharge at high rates; also for lightness, they are provided with as little electrolyte as possible. In consequence, the densities in common use are high, and such batteries are notoriously short-lived.

The quantity of electrolyte necessary for a given cell depends on its ampere-hour discharge, the initial density of the electrolyte, and the terminal density at the end of discharge. This is computed as follows:

From the fundamental equation,

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O,$$

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it is obvious that for each unit of current which is discharged, two electrochemical equivalents of H_2SO_4 must be decomposed, and since the ampere hour equivalent of H_2SO_4 is 1.826 grams, twice this, or 3.652 grams (= 0.129 oz. avoir.), are decomposed for each ampere-hour of discharge. The molecular weight of H_2SO_4 is 98, while that of water is 18, and, consequently, the proportion of water in H_2SO_4 is 18/98, = 0.1837. Assuming that H_2SO_4 is made up of $SO_3 + H_2O$, there are in one oz. of H_2SO_4, 0.1837 oz. of water and 0.8163 oz. of SO_3.

For each ampere hour of battery discharge, there is decomposed, 0.129 oz. of H_2SO_4, of which 0.8163 parts are SO_3; that is, $0.129 \times 0.8163 = 0.1053$ oz. of SO_3, are abstracted from the electrolyte for each ampere hour of battery discharge, leaving behind the original water of dilution in the electrolyte and also that released from the H_2SO_4, which latter amount is $0.129 - 0.1053 = 0.0237$ oz. From these data, the change in electrolyte density can easily be computed. The formula generally used is Fitzgerald's, but this is too cumbersome for general use where frequent calculations are required.

The writer has devised a more simple formula for computing the quantity of electrolyte required, which is as follows:

Let S equal ampere hours discharge;

x equal the quantity of electrolyte required in ounces avoir.;

D equal per cent. of H_2SO_4 in electrolyte at beginning of discharge;

d equal per cent. of H_2SO_4 in electrolyte at end of discharge;

Then Dx = weight of H_2SO_4 in electrolyte at beginning of discharge, and $x - Dx$ = weight of water in electrolyte.

At end of discharge, the amount of water in electrolyte is $x - Dx + 0.0237S$.....(1).

The amount of electrolyte remaining is $x - 0.1053S$.....(2), and the amount of H_2SO_4 is $d(x - 0.1053S)$.....(3).

Also from (2) and (3), the weight of water in the electrolyte at end of discharge is

$$(x - 0.1053S) - d(x - 0.1053S).....(4)$$

Equating (1) and (4) and solving,

$$x = \frac{S(0.129 - 0.10.53d)}{D-d}.....(5)$$

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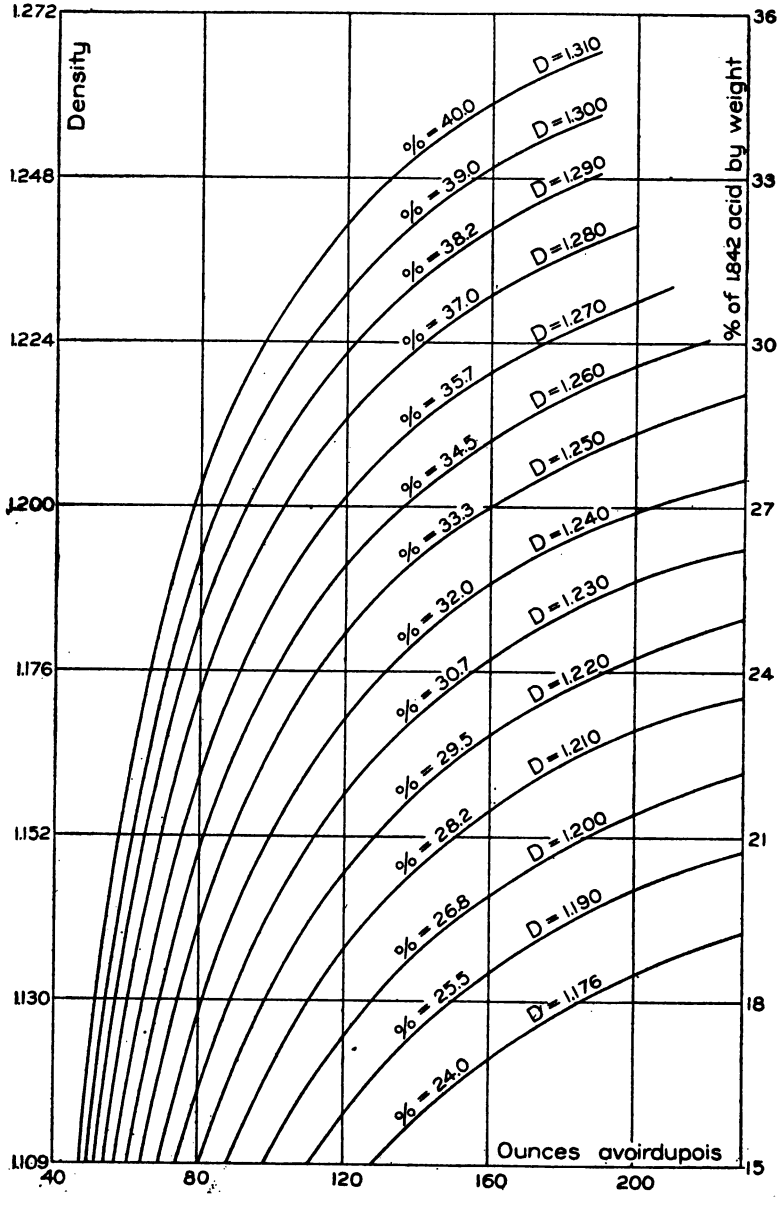

Fig. 2.

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Taking S as 100 ampere hours, (5) becomes

$$x = \frac{12.9 - 10.53d}{D-d} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

If D and d are to be taken as whole numbers and not as decimal quantities, (6) becomes

$$x = \frac{1290 - 10.53d}{D-d} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

For any discharge other than 100 ampere hours, the product of the actual discharge and the value of x as computed, divided by 100, will give the desired quantity of electrolyte.

From the set of curves shown in Fig. 2, the quantity of electrolyte required for any given set of conditions, per 100 ampere hours of discharge, may be read off without computation. Below the intersection of any curve representing initial density, with any horizontal line representing the terminal density, is found the initial weight of electrolyte (at a temperature of 60° F.) required per 100 a. h. discharge, within the two densities selected.

The general practice in this country in regard to initial and terminal densities, quantity of electrolyte per 100 ampere hours, is as given in the table below:

ELECTROLYTE IN STORAGE CELLS.

Initial and Terminal Densities and Quantity.

Averages in United States Practice.

Kind of Plates.	Character of Service.	Discharge Rate	Densities.		Lbs. Electrolyte per 100 Amp. hrs.
			Initial.	Terminal.	
Pasted Pos. and Neg.	Motor Car Propulsion.	4 hours	1.300	1.100	4 lbs.
Planté Pos. Pasted Neg.	General Use—Small sizes	8 "	1.210	1.187	22 lbs.
Planté Pos. Pasted Neg.	General Use—Large sizes	1 " 8 "	1.210	1.777	15 lbs.
Planté Pos. and Neg.	General Use—Small sizes	8 "	1.200	1.180	25 lbs.
Planté Pos. and Neg.	General Use—Large sizes	1 " 8 "	1.200	1.165	15 lbs.

These are only *averages* of general practice. Many storage cells vary appreciably from these data, but the figures given represent good practice.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 1, 1906. President Bancroft in the Chair.

THE ELECTROLYTIC CORROSION OF STRUCTURAL STEEL.

By Maximilian Toch.

Engineers have commented publicly on the electrolytic corrosion of structural steel, particularly those parts known as "grillage beams," supporting columns and base posts which are either in the ground or surrounded by concrete and partly above the ground, with a view to determine beyond question at which of the poles corrosion occurs and whether one pole is more active

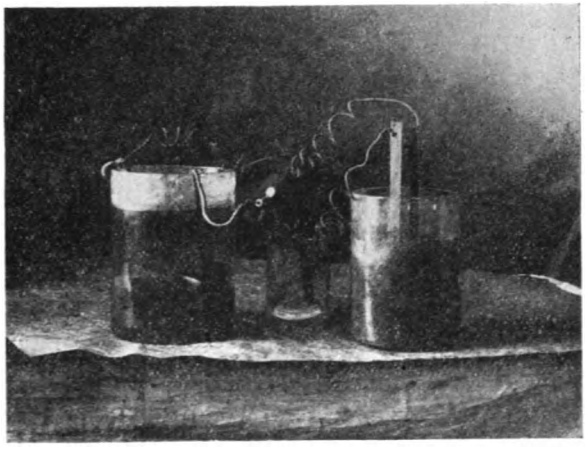

Fig. 1.

than the other. A series of experiments were started since the last meeting, and definite results have been obtained.

The first experiment was performed, as in Fig. 1, by taking two sheets of high-grade watch-spring steel, which is extremely susceptible to corrosion, and connecting them with the ordinary blue stone telegraphic cell. A volt-ammeter was placed in the circuit, and the two pieces of steel buried up to 5 inches in sand. Careful observation was made every day to see that the current was uniform, and the sand was first moistened with salt water,

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and then continually moistened with distilled water, so that the same strength of salt solution was maintained.

This experiment was conducted for one hundred days, and, assuming that the current travels from plus to minus, or from anode to cathode, the anode being connected with the copper and the cathode being connected with the zinc, corrosion was noticed almost immediately at the anode, and the plates showed violent corrosion at the anode and practically no corrosion at the cathode. These plates shown in the illustration indicated some slight corrosion on the cathode, which, however, was principally chemical corrosion.

The strength of the current was .05 of a volt, and the distance between the plates, in the damp sand, was 1½ inches, and the amperage varied from .02 to .05.

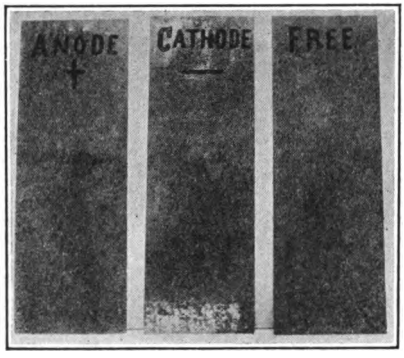

Fig. 2.

The current was measured by a "Pignolet" direct reading, continuous current, volt-ammeter, and the amount of current which produced this corrosion was exceptionally small.

The next experiment was tried in exactly the same manner, for a shorter period of time, but instead of using two plates, three plates were used, the third one being designated as the "free" plate in which chemical corrosion had full sway. At the end of six days, these plates were removed; the anode, as shown in Fig. 2, showed marked corrosion, the cathode plate showing practically no corrosion at all, and the "free" plate showed a fair average between the cathode and the anode, and it can be deduced that the difference between the cathode

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and the anode corrosion is equal to the "free" corrosion. In other words, there is many times more corrosion on the anode than there is on the "free" plate, and no corrosion on the cathode plate.

The plates were very carefully varnished all over to preserve them, after the experiments were completed. The rust produced was first the green ferrous oxide [$Fe(OH)_2$] which, being a very unstable product, was quickly converted in the air into $Fe_2O_3H_2O$.

The current which produced the result was .1 of an ampere at .1 of a volt. The salt solution was four times as strong as that produced in the first experiment.

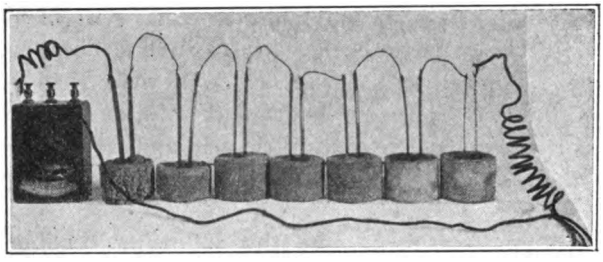

Fig. 3.

The third experiment, shown in Fig. 3, was, however, of the greatest importance, owing to the fact that the author attempted to imitate the conditions as they existed in buildings. The same kind of steel was taken and imbedded in various mixtures of concrete, starting from neat cement and going up to 1, 3, 5.

There is a well-known law in physical chemistry that reactions which take place with an increase of pressure are retarded by an increase of pressure, and the question has come up as to whether it is possible for steel to corrode when surrounded by concrete, many engineers holding that the alkaline nature of the cement will prevent the corrosion, and others holding that in conjunction with this condition, the pressure exerted by the concrete prevents chemical decomposition. The author is glad to be able to throw some light on this subject, and the following experiment was carried out:

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In the first place, cement was taken of known composition, agreeing practically with the definition as quoted in the Journal of the American Chemical Society,[1] when the question of the permanent protection of iron and steel by means of cement was thoroughly gone into. The cement for these experiments was what might be termed the tri-calcic silicate and calcium aluminate. This is in contradistinction in the general classes of Portland cements containing dicalcium ferrite as a part of their composition and free calcium sulphate in excess.

A cement of the calcium aluminate class free from iron and free from calcium sulphate is a well known protector of steel in these experiments. The pieces of steel were connected up with six elementary cells of sufficiently high voltage and amperage, and it was impossible to get a direct reading from the volt-ammeter, the instrument being too sensitive. The seven pats containing the steel strips (see Fig. 3) were then put into the circuit and wet every few hours with solutions of 5 per cent. sodium chloride and 1 per cent. nitric acid and water, in order to increase their conductivity and produce corrosion as rapidly as possible.

The volt-ammeter then gave the following reading: The average strength of the current was .05 amperes at .05 volts throughout the entire experiment. Corrosion was immediately noticed on the anode pole, and the pat made of neat cement, which should have protected the steel most perfectly against all kinds of corrosion, showed a hair-line split colored with rust at the end of the third day, which demonstrated that the chemical reaction of rusting had taken place at the anode; that the molecular increase had likewise taken place, and the pressure caused by the molecular increase had split the block.

The steel in each alternate pat was painted half the length, which was embedded in the cement with an insulating paint of known composition having a voltage resistance of 625 volts per millimeter. The results obtained after these various briquettes were broken open, demonstrated that electrolytic corrosion takes place most violently at the anode, unless the steel be coated with an insulating medium.

Cement, concrete, or even neat cement, is therefore no pro-

[1] Vol. XXV. No. 7, 1903.

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tection against electrolytic corrosion, unless the steel be insulated as heretofore mentioned, and there was absolutely no corrosion where coated with such insulating material. It must be noted that the cathode in all these experiments was perfectly free from any signs of oxidation.

The result of this entire series of experiments is to prove conclusively that electrolytic corrosion of structural steel embedded in concrete or sand takes place only at the anode, and there with great violence; and furthermore, that the cathode is protected by the electrical current. The popular impression that cement is a protector against corrosion of all kinds is fallacious, and that the anode does not only rust very violently, but a molecular increase of volume may take place which will split the concrete shell.

Another conclusion arrived at is that the electrolytic rusting of "grillage beams" of buildings need not be feared if the structural steel be protected by a good insulating material; but the insulating medium should form a bond with concrete.

DISCUSSION.

DR. WM. H. WALKER: I did not understand whether there was an external source of electricity between the two terminals, or whether the cup itself formed the battery.

MR. TOCH: The briquettes were connected up with the six elementary cells and the voltameter placed in the circuit.

MR. HUGH RODMAN: Did the current vary during the test?

MR. TOCH: The briquettes and the sand were wet every day. I will read that particular part from my paper: "Careful observation was made every day to see that the current was uniform." There was practically no variation in the current. We did not permit it.

MR. RODMAN: In regard to those buildings already constructed and having no protection, would it not be possible to make them cathode by some external source, so as to keep them from rusting and then to put cement around them?

MR. TOCH: Yes sir, that is done, too; and I am very glad to say that a number of engineers are keenly alive to the subject

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of corrosion. It is often possible to get at the foundation beams, clean them thoroughly, paint them properly and then put a heavy coat of cement around them. As to how far it may be possible to make a building cathode by some external source I cannot say.

MR. CARL HERING: In this connection I might repeat something I suggested some years ago on a similar occasion. If a mass of zinc be buried in the moist earth near the foundations where the steel is apt to corrode, and if this mass of zinc be connected electrically with the base of the structure, then, if any so-called positive currents flow to earth, making the foundation anode, they will flow to ground through the zinc in preference to flowing through the iron; hence the iron structure will then be protected against corrosion caused by these positive currents. Reverse currents will flow into the steel in preference, and will tend to clean and preserve the steel. During the time when there are no currents flowing down the structure into the earth, a local current will tend to flow from the zinc through the earth, up through the structure and back through the connecting wires; the effect of this current will be to keep the iron structure reduced and therefore clean. The zinc will therefore be acting in a beneficial way whether there is a current flowing or not. It seems to me this would be a very cheap and effective way of not only preventing the further corrosion of the base of steel structures, but would even tend to reduce the corrosion that may have already taken place. Of course, this block of zinc will have to be examined from year to year, to see whether it is still there or whether it has been consumed and needs to be replaced.

PRESIDENT BANCROFT: Isn't there a possibility that there may be a leakage of current from one cathode to another cathode, in which case you would be introducing more damage than you are checking? It seems to me that such a case might easily arise where there was a marked difference of distance between the anode and one or more cathodes.

MR. C. E. ACKER: What is it that makes any part of the iron structure of a building the anode? How does it become an anode?

PRESIDENT BANCROFT: We have an outside source of current and a zinc anode. Let A, B and C be iron beams which are to

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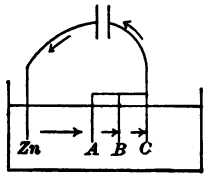
act as cathodes. There is always a possibility of A and B acting as intermediate electrodes. In that case there will be corrosion. I do not know whether that can actually occur in a



steel building but such a state of things is certainly not impossible, I know.

MR. S. S. SADTLER: It would take nearly 2 volts to jump there.

PRESIDENT BANCROFT: Not with both of the beams iron.

MR. SADTLER: I should think it would. It would not take exactly 2 volts.

PRESIDENT BANCROFT: It would if the iron did not corrode; but it would not if the beams corroded.

MR. SADTLER: I should think it would in any case. It would with lead, which is an analogous case as both would form oxides at the anodes.

PRESIDENT BANCROFT: With lead we have peroxide formed at the anode in a sulphate solution while iron forms soluble ferrous sulphate.

MR. ACKER: Is there any question of external currents?

PRESIDENT BANCROFT: In the case cited by Mr. Toch, as I understood it, they were introducing the external source of current in order to keep the iron beams cathodes and therefore prevent their corrosion. If that current gets too high or there is a fault in any way where the beams are connected there is always the possibility of a cross leakage.

MR. ACKER: Whenever there is corrosion due to electrolysis it would seem to be desirable first to remove the cause of the difficulty, then adopt such measures as would prevent its recurrence, if possible, and to paint afterward. I certainly should use the best paint in any case, but it does seem desirable to head off the stray currents of electricity which produce the electrolytic

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corrosion. I do not know the source of all of the currents which cause electrolytic corrosion of the structural iron and steel in foundations and buildings. I should imagine that the cause could be found and eliminated.

Several years ago I was conducting an investigation into the cause of a very heavy gas leakage in one of the Gas Company's underground mains in the upper part of New York City, in which territory several lines of electric railway had recently been built. These lines of railway were not built as carefully as they are nowadays, and not everything was properly proportioned for the distribution of the current, and particularly, for the return, so to speak, of the current to the power house. One or two badly corroded sections of gas mains were accidently discovered, and caused a fear that much of the increased gas leakage was due to electrolytic corrosion, so I investigated the system of pipes in the upper part of the city for some time, and obtained interesting results. I had a map of the territory showing location of gas mains, water mains and street railway lines. With the assistance of a few men I started out with instruments, and, beginning at a point near the power house ascertained whether the street gas lamps and water hydrants at each corner along the railway lines were positive or negative to the surrounding earth, that is to say, whether the current was leaving the gas and water mains at that point or entering same. At several street intersections excavations were made in order to get at the gas mains, and obtain this information. A great number of readings were obtained in this way, so that I was finally enabled to make a map which indicated that a great portion of the system of gas mains was being utilized, to a certain extent, in lieu of the rails and return feeders for the current to get back to the power house. In general the system of gas pipes and water pipes at considerable distances from the power house was either neutral or negative to the earth, that is to say, if any current at all was passing it was going from the earth to the pipes. Under these circumstances no corrosion could be expected, and, as a matter of fact, was not observed. Several miles of pipe, however, running parallel to the railway system, and leading in the general direction of the power house was found to be positive to the earth, and therefore subject to electrolytic corrosion. In several cases where these pipes came relatively close

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to the trolley lines very serious corrosion was noticed. One pipe, which crossed the street underneath the railway tracks, was found to be eaten entirely through, and was perforated with holes aggregating several square inches from which the gas was escaping to a large extent. Many other seriously corroded gas pipes and leaks were found in this way. I judged that the rail bonds, or I should say, the bond connections, were not sufficiently good to carry the current back to the power house, without a considerable proportion of it being diverted to the pipes over a considerable area, which it followed in the general direction of the power house, and then left these pipes again to enter the ground again and get back to the rails.

The gas company did not object seriously to the current entering and passing along the pipes but it did object to the current *leaving* the pipes.

I found one serious condition of affairs at a certain street crossing on the railroad line. My readings indicated that the current was entering the gas pipes on one corner of the street, and that it was leaving the water main on the other corner, as indicated by the instrument attached to the street hydrant and the ground, in the one case, and the street lamp and the ground, in the other case. I excavated to get at the gas main at this opposite corner and found that the current was *leaving* the gas main also, which was just opposite to the direction of the current on the other corner of the same street where it was *entering* the gas main. This seemed strange, but it was easily understood when we discovered later on that the copper bonds had become disconnected, or had been cut at this point on the railway line so that on one side of this point the current left the rails, passed through the earth to the pipes, which it traversed for a considerable distance, but part of the current began to leave the pipes on the other side of the street to re-enter the rails beyond the break. Wherever the current had been passing from the gas pipes to the earth for a considerable time, certain sections of pipe could be found which were badly corroded or perforated. This entire difficulty was largely remedied afterward by the Street Railway Company improving the bonds all along the track, and furthermore by carrying some heavy return feeders to different sections of the track, so that there was less tendency for the cur-

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rent to leave the rails and follow the pipes for a certain distance in seeking the path of least resistance.

In course of time, after these improvements had been made, the pipes were hardly positive to the earth at any part of the entire system, and I don't think there has been any considerable amount of electrolysis since. The difficulty, which was undoubtedly serious at one time was overcome by eliminating the source of the trouble, and that is the point which first occurred to me in connection with Mr. Toch's paper in relation to the preservation of I-Beams and structural steel work in general in buildings.

If it is found that there is corrosion due to electrolysis I should imagine that it would be wise to ascertain the source of the current and remove the cause of the difficulty instead of painting the entire work for the purpose of preventing it. I would repeat what I said before, however, that I should consider it wise to put on the best paint obtainable in any event.

MR. CARL HERING: I would also like to call attention here again to the fact that it is not at all proper to assume that because there is a great difference of potential between two underground pipes, there necessarily is a large current flowing, and *vice-versa.* It may be so, but it is not necessarily so, at all, in fact it is more likely to be the very reverse. If, for instance, two pipes are buried in dry earth and are thereby absolutely insulated from each other, and if they are connected to the two poles of a source of current, they will show the highest difference of potential and yet there will be absolutely no current; whereas if they are inserted in very good conducting ground, there would be practically no difference of potential between them and yet the maximum current would be flowing. It seems to me therefore that it is quite incorrect to simply measure the potential difference between two underground pieces of metal and then conclude, as is often done, from that alone that current is or is not flowing, or to assume that the measure of the potential is a measure of the current that is flowing, because it is more than likely to be absolutely wrong.

Some years ago when on a similar occasion, I suggested using a piece of zinc in the way I described a moment ago, an electrical engineer who had acted as a court expert in such cases as this

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said, that he had already tried that method and that it had not been successful; but he added that it was cheaper to use iron instead of zinc, so he had used iron! He had missed the very point which I tried to make by suggesting the use of zinc, yet he was an expert, who gave testimony in the courts, on the electrolysis of underground pipes. It was a good illustration of the importance of a knowledge of one of the first principles of electrochemical actions.

DR. RICHARDS: Since the pipes are usually wrought iron, the use of steel could not be altogether purposeless, as a way to protect wrought iron. I believe steel has been used to protect wrought iron from corrosion because it corrodes much more easily than the wrought iron.

DR. C. S. PALMER: Do you know, Mr. Hering, whether zinc alone will protect iron in such cases, without the use of any external current?

MR. HERING: Yes, it will do it very effectively, though slowly. I have used this method in my shop; when tools got very rusty I connected them electrically to a piece of battery zinc, and laid them in dilute acid for a few days or a week, after which the tools would come out perfectly clean.

DR. PALMER: Speaking with regard to the protection of buildings?

MR. HERING: If it will do it on a small scale it certainly should do it on a large scale, but of course it is done at the expense of the zinc. The zinc which is consumed can however be readily replaced, while the steel columns cannot.

DR. PALMER: Have you anything in dollars and cents as to the cost of the zinc in protecting a building?

MR. HERING: No, I have not; but I should think such buildings were worth so much money that the question of a few dollars worth of zinc would not be of any consequence. It may be that aluminum would do the same thing; but I am not sure.

DR. RICHARDS: The galvanizer's dross carrying 5 to 10 per cent. of iron is much cheaper than pure zinc and because of its composition it acts more efficiently than pure zinc; it is more easily disintegrated and it is used by preference, I believe, in boilers, for galvanically protecting them, because of its being more easily disintegrated.

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MR. HERING: I cannot agree with Dr. Richards that it is more effective in this action because it is more easily disintegrated; if iron and zinc are intimately mixed together, there is necessarily an energetic local electrochemical consumption of the zinc because it is mixed with the iron; this constitutes the energetic action to which Dr. Richards referred, but this is not at all the action which is desired; the latter would become even *less* intense thereby; so it seems to me the purer the zinc, the better it would be for this particular purpose.

PRESIDENT BANCROFT: Doesn't this matter of protecting iron by zinc run back to Sir Humphry Davy at the beginning of the nineteeth century? My impression is that he introduced that in the first or second decade of the century.

MR. HERING: It is all the more surprising that it is not more generally known.

DR. PALMER: I think some of the old engineers more familiar with New York City work can complete this statement better than I can; but a friend of mine a few years ago told me that the iron sheathing on the wharves were protected by an old Irishman, who found out that he could use zinc nails, and did so for several years.

PRESIDENT BANCROFT: What becomes of the iron sheathing when the zinc nails become corroded?

DR. PALMER: Presumably the zinc nails were replaced as fast as they were consumed. It was told to me by an engineer, Major Henry Fulton, now deceased.

PRESIDENT BANCROFT: I can quite understand that it might protect the iron for a while; but I should think that later you would need a dredging outfit to recover the sheathing.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, held at Ithaca, N. Y., May 1, 1906, President Bancroft in the Chair.

ON THE PHYSICAL PROPERTIES OF FUSED MAGNESIUM OXIDE.

By H. M. Goodwin and R. D. Mailey.

In connection with a recent interesting note from the Königlichen Porzellan Manufaktur[1] on the manufacture of tubes, crucibles, etc., of pure oxide of magnesium, we have thought that the results of various experiments on the physical properties of this substance after it has been actually fused, which have been carried on recently in the Electrochemical Laboratory at the Institute, may prove of some interest.

Our attention was first directed to the preparation of fused oxide of magnesium in an attempt to find a substance which at temperatures up to at least 1,000° C. would serve as suitable containing vessels for fused salts in an investigation now in progress on their electrical conductivity, *i. e.*, a substance which would possess the properties of being chemically inert, a non-conductor of electricity, and having a sufficiently high melting point to retain its shape at the temperatures mentioned. A small coefficient of expansion was also desired. We were particularly desirous of obtaining tubes or rods of such a substance. Whether the material described by the Charlottenburg firm is magnesia which has actually been fused or not is not quite clear. It seems highly improbable, however, that tubes of the fused material 80 cm. long and 7 cm. in diameter and crucibles 50 cm. high and of any diameter have been made. These are probably moulded under pressure from powdered magnesia, and then heated to a very high temperature.

After experimenting with a number of silicates and metallic oxides both in the natural crystalline form and artificially prepared, in the hopes of finding a satisfactory material, it was decided to try to make pure fused magnesium oxide. That this should be possible in the electric furnace seemed probable, as Moissan states that the carbide is not formed when the oxide is

[1] Zeitschrift für Electrochemie, Vol. 11, p. 581 (1905).

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heated with carbon. The first attempt was made in a graphite-resistance furnace. A pure Acheson graphite rod 18 inches long and ¾ inch outside diameter was bored with a ½ inch drill and the ends fixed into large graphite block terminals for leading in and out the current. The furnace was mounted vertically, packed with coke to prevent excessive oxidation of the graphite tube and the whole heat insulated with fire brick. The furnace was heated by current from a 50 K. W. transformer, the voltage of which could be varied by steps of 10 volts from 160 volts to 10 volts. From 20-30 K. W. were used in the furnace to maintain the temperature required. Chemically pure magnesium oxide was fed in at the top of the furnace in the form of powder, and packed down by means of a graphite rod. In this way it could be melted, and rods of the fused oxide were obtained about ¼ inch in diameter and 2 inches long.

In no case, however, could rods be formed as large as the interior diameter of the bored graphite rod, owing to an action between the oxide and either the walls of the tube or gases given off from or diffusing through the walls of the enclosing tube. This was indicated by the formation of a volatile product which condensed to a black mass in the upper cooler portions of the furnace. To prevent this substance from completely stopping up the furnace it was found necessary to bore lateral holes through the graphite tube in the hottest zone, at which condensation could not take place. The composition of the substance condensed in the cooler part of the furnace was not determined, although tests indicated that it was not a carbide. Treated with acid, hydrogen sulphide was always evolved, showing that impurities from without the furnace proper, probably in the coke, must have diffused through the graphite to the oxide within. The graphite rods were tested and found to be very pure, having been especially prepared for this work through the kindness of the Acheson Graphite Co., of Niagara Falls.

As it was found that rods of magnesia of the desired size could not be obtained by the method above described (at least when carried out on the scale feasible at the time), it was thought that an arc furnace might be more effective. A hollow rectangular graphite boat 10 x 4 x 4 cm., was used as a receptacle for the fused oxide. Over the center of this was arranged a powerful alternat-

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ing current arc into which the oxide was fed from above. The whole was enclosed in graphite bricks, around which were built up fire bricks. In this way irregular masses of the fused oxide, as large as one's hand, were obtained, and from such masses, rods or pieces of the desired length were bored by means of carborundum. The large masses thus obtained were not, however, homogeneous. Certain portions or layers were composed of very fine compact crystals resembling marble; other portions were composed of larger crystals. Some excellent samples were obtained, however, so hard and compact that they were quite non-porous to water and to fused salts. The great difficulty experienced was in getting pieces sufficiently free from tiny bubbles or blow holes. Up to the present time we have been unable to completely eliminate these in pieces larger than two or three cubic centimeters. If the process were to be carried out on a much larger scale and a larger mass of oxide brought to state of quiet fusion and then cooled, better results could undoubtedly be obtained.

PHYSICAL PROPERTIES.

Appearance.—The fused oxide when pure and uncontaminated with particles of graphite, is a pure white, very hard crystalline substance. The fused surface resembles glazed porcelain. Depending upon the rapidity of cooling, the crystals appear either very minute and compact, giving the structure the resemblance of marble; or fairly large and compactly arranged in layers. The substance takes on a good polish.

Hardness.—The fused oxide is exceedingly hard. Its hardness was found to be between that of apatite (transparent variety) and feldspar (white cleavable variety), although nearer the former than the latter.

Specific Gravity.—This was determined by the Archimedes method from a number of selected samples, the following values being obtained:

Sample A. Mean value of three small cylinders (used for expansion experiments), at 19° C. 3.485.

Sample B. Mean value of large cylinder 5.5 cm. x 1.2 cm. diam., at 20° C. 3.562.

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Sample C. Mean value of four small irregular pieces at 20° C. 3.432.

Mean of A, B, C., at 20°C., 3.493.

The specific gravity of the mineral periclase consisting of crystalline magnesium oxide and a little ferric oxide, of the percentage composition,

MgO	FeO
93.86	5.97
93.38	6.01

is given as 3.674.

Melting Point.—The melting point was determined by putting two or more small fragments of the already fused oxide into a graphite tube resistance furnace, holding the current in the furnace constant, and determining the temperature of that part of the tube where the samples were placed by means of an optical pyrometer. If after a run the pieces were found to be fused together, the melting temperature was considered to have been exceeded. Thus by making a number of runs temperature limits were determined between which the melting point lay.

The furnace consisted of a 11-inch graphite tube, 1 inch in diameter, and bored out to ⅝ inch inside diameter. Midway between the ends was a ⅝ inch hole, opening laterally into the bore of the tube. The ends of the tube were attached to graphite terminal blocks, 6 inches square and 3 inches thick. The opening in which the sample to be fused was placed was viewed through a larger hollow graphite tube placed at right angles to the furnace tube. To prevent too rapid oxidation of the furnace the tube was surrounded with fine coke and magnesia powder, which was held in place by fire bricks and asbestos. By this arrangement, when the furnace was heated, the pyrometer could be sighted through the horizontal side tube at the opening in the heating tube, and the conditions for "black body" radiation were approximately approached. In this furnace temperatures from 1,500° to 2,500° could be maintained with currents ranging from 300 to 700 amperes. The desired regulation of the current was obtained by an adjustable rheostat in the field of a 25 K. W. low voltage D. C. generator.

The temperatures were measured with a Wanner pyrometer,

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which had been calibrated at the Reichsanstaldt. This pyrometer had a range from 900° C. to 2,000° C., which could be increased to 4,000° C. by means of an auxiliary smoked glass screen.

The samples whose melting points were determined were fragments of magnesium oxide which had been previously fused. In every measurement the samples were placed near the side opening in the furnace tube, so that they were in line with the pyrometer. By this means the temperature of the graphite tube with which the samples were in contact was the temperature measured.

From the series of measurements made, it was found that below 1,890° C. the fragments did not fuse together or soften. Above 1,940° C. they always fused together. This indicates that the melting point of magnesium oxide (fused) is between 1,890° C. and 1,940° C. In round numbers 1,910° C. may therefore be taken as the approximate melting point of the oxide.[2]

Electrical Conductivity.—The electrical conductivity of the fused oxide was determined as follows:

A small cylinder 8 mm. thick by 14 mm. diameter, was first prepared by very carefully grinding its surfaces. This was placed between two pieces of thin platinum foil (A), which were pressed against the sample (B) by graphite rods (C). These were held in an iron frame, as shown in Fig. 1. The upper graphite rod was insulated at the top by a piece of fused magnesium oxide D, whose resistance was maintained practically infinite by keeping it outside of the furnace, and consequently cool. To insure nearly constant pressure on the sample B during the heating, a lever (E) and spring (F) were used, as shown. The whole arrangement of this apparatus was freely suspended from an insulated stand in a vertical cylindrical electric furnace of the platinum resistance type. The 110 or 220 volt circuit was connected to the graphite rods C by means of platinum leads.

The sample to be tested and the graphite rods were connected in series with a Weston voltameter across the 110 (or 220) volt D. C. mains. The resistance under investigation being very much greater than the resistance of the voltameter itself (15,800 ohms), the latter could be used as an ammeter and deflections for a con-

[2] We hope to fix the melting point of this and some other refractory oxides with a higher degree of precision than here attempted, shortly.

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stant applied voltage assumed proportional to the current. Hence if

R = resistance of sample.

R_v = resistance of voltameter = 15,800 ohms,

V = reading with voltameter alone in circuit, *i. e.*, the voltage across mains.

v = reading with voltameter + magnesia sample in series.

then

$$R = R_v \frac{(V - v)}{v}$$

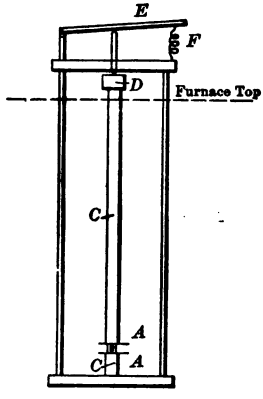

Fig. 1.

The temperature was measured by a thermo-electric junction (platinum, platinum-Rhodium), which was calibrated at the sulphur, aluminum, and gold points.

The values of the specific conductivity of the magnesium oxide in reciprocal ohms at various temperatures are given in Table I and on the accompanying plot. These values should be considered as maximum values, as slight traces of graphite remained in the sample in spite of the fact that it was heated repeatedly to near its melting point.

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TABLE I.

SPECIFIC CONDUCTIVITY OF FUSED MAGNESIUM OXIDE.

Temperature.	Specific Conductivity.
700°C	
800	0.01×10^{-6}
900	0.10 "
1000	0.20 "
1050	0.34 "
1100	1.00 "
1150	2.60 "
[8][1500	85.0×10^{-6}]

[8] Nernst-Reynolds-Landolt and Börnstein Tables.

For comparison, the conductance of samples of Berlin and Meissen porcelain (glazed) were also measured in the above apparatus, and the values obtained are given in Table II, and also on the plot. The results show that magnesium oxide is a much better insulator than porcelain at temperatures below 1,100° C. Above that temperature the large temperature coefficient of the oxide indicates that its conductivity probably becomes greater than that of porcelain.

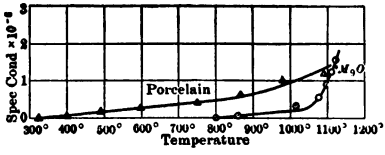

FIG. 2.

TABLE II.

SPECIFIC CONDUCTIVITY OF PORCELAIN.

OBSERVED VALUES.			VALUES BY	
Temp.	Berlin.	Meissen.	Foussereau.[5]	Nernst-Reynolds [6]
50°C	. . . . .	. . . . .	0.465×10^{-15}	
200°	. . . . .	. . . . .	0.746×10^{-10}	
400°	0.05×10^{-6}	0.05×10^{-6}		
500°	0.20 "	0.10 "		
600°	0.32 "	0.18 "		
700°	0.43 "	0.24 "		
800°	0.55 "	0.40 "		
900°	0.75 "	0.70 "		
1000°	1.00 "	0.94 "	. . . . .	3×10^{-5}
1100°	1.30 "	1.27 "		

[5] Landolt and Börnstein Tables.
[6] " " "

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Our measurements, which were made with direct currents, indicated distinct polarization in the case of porcelain, but with the oxide no trace of such action was evident.

Coefficient of Expansion.—This was determined by Mr. G. W. Eastman[1] by the Fizeau method, using the latest form of Abbe-Fizeau Dilatometer manufactured by the Zeiss Optical Co., of Jena. The interference apparatus was similar to that used by Reimedes, and consisted of two quartz plates, A and B, cut perpendicular to the optic axis. The samples of fused magnesium oxide used consisted of three small carefully ground cylinders, D, 7.4 mm. long and 2.5 mm. diameter, which served to support the upper quartz plate upon the lower, as shown in Fig. 3. These supports were placed at the vertices of an equilateral triangle. The interference fringes were produced between the upper surfaces of B and under surface of A. The coefficient of expansion of D could be at once computed from the shift of the fringes due to a measured change in temperature.

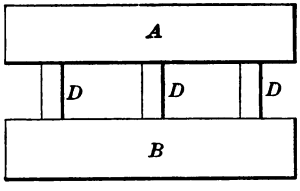

Fig. 3.

The heater consisted of a massive casting of copper, so bored that the interference apparatus could be placed at the center and observed by means of a total reflecting prism from the outside. The temperatures were measured by a very carefully calibrated platinum resistance thermometer, and extended over a range from 120° C to 270° C. The value for the linear coefficient of expansion over this range of temperature was found to be

$$\alpha_t = 10^{-8} \left[1140 + 0.92 \, (t - 120°) \right]$$

This value is not much greater than that for quartz crystal cut parallel to its optic axis, and is nearly equal to that of platinum, as will be seen by comparison with the following data:

[1] Thesis Mass. Inst. of Technology, (1904).

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Quartz Crystal.

Randall :[1] $\alpha_t = 10^{-8}$ [717.0 + 1.620 t] for temperatures to 250° C.

$\alpha_t = 10^{-8}$ [1125.0 + 1.65 (t −250) + .00566 (t −250)2 + .0000134 (t −250)^3] for t = 250° to t = 470°.

Reimerdes :[2] $\alpha_t = 10^{-8}$ [692.05 + 1.689 t] for t = 5° to t = 220°

Eastman :[3] $\alpha_t = 10^{-8}$ [698.7 + 1.580 t] for t = 85° to t = 235°

Fused Quartz.

Holborn & Hening :[4] $\alpha t = 54.0 \times 10^{-8}$ for t = 0° to t = 1000°

Platinum.

Holborn & Day :[5] $\alpha_t = [\ 8889 + 1.274\ t\ ]\ 10^{-9}$ for t =0° to t = 1000°

Le Chatelier :[6] $\alpha_t = 1130 \times 10^{-8}$ for t = 0° to t = 1000°

The close agreement between the value of the expansion coefficient of fused magnesia and that of platinum should prove a valuable property in the construction of apparatus involving joints of these two materials. We have found in fact that platinum caps ground to fit the ends of rods of the fused oxide remain tight over wide ranges of temperature.

Heat Conductivity.—The heat conductivity has not been determined in this laboratory. In a recent table of thermal conductivities or refractory materials published by Messrs. Hutton and Beard,[7] however, "Magnesia (fused)" is included, the conductivity of this material in the form of granular powder (600 meshes per sq. cm.) being given as K = 0.00047 as compared with K = 0.00029 for lime, and K = 0.00028 for fire brick. No details regarding the preparation of the magnesia are given by the authors.

Chemical Properties.—Fused magnesium oxide possesses in a remarkable degree the ability to withstand chemical action of

[1] Physical Rev., *20*, 10 (1905).
[2] Inaug. Diss. Jena (1896).
[3] Thesis Mass. Inst. Tech. (1904).
[4] Ann. der Phys., *4*, 446 (1903).
[5] Ann. der Phys. *2*, 508 (1900).
[6] Landolt & Börnstein Tables.
[7] Proceedings of the Faraday Society, *1*, 266 (1905).

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many neutral salts at high temperatures, and is therefore well adapted for use as vessels and apparatus for containing such salts when subjected to high temperatures. Qualitative tests of the chemical action of various fused salts on the oxide gave the following results:

Silver, sodium and potassium nitrates, sodium and potassium chlorides, bromides and sulphates, zinc chloride and barium nitrate showed no action on a polished sample of the fused oxide, when the latter was heated for an hour or more in the fused salt. Barium chloride had a very slight action; sodium carbonate, potassium sodium carbonate, potassium hydrate and cryolite attacked the fused oxide energetically.

Dilute hydrochloric, nitric and sulphuric acids attack the fused oxide in the cold slowly. Concentrated acids are less active than dilute acids.

Electrochemical Laboratory,
Massachusetts Institute of Technology.

DISCUSSION.

MR. HERING: I have been very much interested in this paper, and would be very glad if there were more papers on such subjects. I would also like to see this one extended in its scope. It is information of this sort which is of great value to the practical engineer.

There are, however, some criticisms I wish to make. In Table I they give what they call the specific conductivities, but unfortunately they forget to state in what unit these figures are. The figures are therefore valueless except for their relative value, unless a person will take the trouble to figure out, as I have done, what the probable unit is. In this way I have found that probably the unit which they mean is the meter, square millimeter, reciprocal ohm unit; otherwise the figures would be so abnormal that they could not possibly be correct. I would suggest that it would be very desirable to have authors of the papers in our Transactions state in what units their figures are. The only thing these authors say about it is, that they are in reciprocal ohms; that is

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insufficient, because it might refer either to reciprocal ohms and cubic centimeter, which is one standard of conductivity, or to the reciprocal ohm, meter, and square millimeter standard. The latter appears to be the one used by them.

I was sorry to see that the experiments were not continued to a higher temperature, because when magnesia is used in furnaces it is generally because there is a very high temperature and then it is apt to become electrically conducting; we therefore should like to know how well it conducts then. I have worked out some figures and find that the last figure given in this table, for 1500°, makes that material conduct electrically roughly about 1-700,000th as well as copper; in other words the resistivity is roughly about 700,000 times the resistivity of copper, provided my assumption is correct as to the unit which they used; I think it is.

PRESIDENT BANCROFT: Copper at what temperature?

MR. HERING: Copper at ordinary temperatures. In order to compare this figure with the one for the Nernst lamp filament, I worked out the latter. My figures are only very crude, as I had only very rough data: in the Nernst lamp filament I found that the resistivity is roughly about 0.66 ohm per cubic centimetre, which is about 400,000 times that of copper. Or about 6,640 in meter, square millimeter, ohm, unit of resistivity.

If the conductivity unit used in Tables I and II is what I suppose it is, namely the meter, square millimeter, reciprocal ohm unit, it will aid one in obtaining a conception of this unit to say that in this unit the conductivity of copper is roughly about 60., while in the cubic centimeter unit it is about 600,000. In resistivity units this figure is 0.01667 in the meter, square millimeter unit or 0. 000,001,667 in the cubic centimeter unit. The conductivity of the Nernst lamp filament above referred to would be about 0.00015 in the meter, square millimeter unit, or 1.5 in the cubic centimeter unit.

The electrical conductivity of magnesia or other firebrick materials may become quite important at high temperatures. Some time ago, when designing an electrical resistance furnace, I made a calculation to determine this; assuming that the ordinary firebrick, 2x4x8 inches, was made of the same material as the Nernst lamp filament and that it was raised to the same tempera-

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ture, then the resistance along the long dimension (8 inches) is only about one-quarter of an ohm. This is sufficiently low to shunt away considerable current from the resistor, but it is not likely that the lining of a furnace would be raised to the same temperature as that of the Nernst lamp filament; these figures are therefore of use only as a general guide.

I also would like to endorse the statement that impurities in the magnesia make a very great difference in the conductivity. I made a Nernst lamp filament with pure magnesia alone, and found that I could not make it conducting, although I heated it to the temperature of melted platinum; but the moment impurities are introduced it becomes very conducting. It is likely therefore that firebrick made of commercial magnesia would be very much more conducting than the presumably pure magnesia which the authors used in their experiments.

I might add that Heraeus made a statement that at 1500° to 1600°C. porcelain conducts injuriously; by which I suppose he means that porcelain cannot be depended upon as an electric insulator in a furnace; this is not such a very high temperature.

Near the end of this paper the authors give the value of a constant K, but unfortunately they do not state what units it is given in, and therefore it is valueless to engineers.

PRESIDENT BANCROFT: We have recently received some pure magnesia articles from Germany; and I thought it might be interesting to have them here for inspection in connection with this paper. I have a crucible, a large tube, and a small thermopile tube that have been sent to us. I have here also some photographs of sublimed magnesia sent by Messrs. Fitzgerald and Bennie. In connection with the statement of Mr. Hering in regard to the conduction of porcelain at high temperatures, I have understood that Mr. Eddy built a resistance furnace at one time which consisted of a porcelain tube as the resistance material and that he got temperatures above the fusing-point of platinum without any difficulty.

MR. HERING: I wish to file a protest here against the continuation of the use of the term "specific conductivity," which is entirely incorrect, although not infrequently used in the older literature. It ought to be either "conductivity" or "specific conductance." It is synonymous to the terms "resistivity," or "specific

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resistance;" we never speak of "specific resistivity," then why say "specific conductivity." To do so would be like speaking of a gaseous gas, or of a liquid fluid. Conductivity is specific in itself and does not require the word "specific" before it.

MR. C. F. CARRIER, JR.: Did the authors make any comparison between the chemical action of fused salts on their fused magnesia and on the form of magnesia of which commercial magnesia bricks are made? In practice there will be no use in using an expensive material like fused magnesia to resist chemical action if a magnesia brick would resist chemical action to perhaps practically the same extent.

DR. WALKER: I have no data on the subject.

(Communicated after Adjournment.)

F. A. J. FITZGERALD AND P. MCN. BENNIE: Since a great many experiments on the fusion of magnesium oxide have been carried out at our laboratory, it may be of interest to give some of the results we obtained in connection with this paper.

The purest specimen of fused magnesium oxide in our possession was obtained from Germany some five years ago. It was made by fusing pure magnesium oxide in an electric furnace. On analysis, it was found to contain 99.5 per cent. MgO, and to have a density of 3.572 at 20° C., compared with water at 4°.

We have prepared in our laboratories, a large quantity of fused magnesia, using a good grade of calcined magnesite as the raw material.

The first experiments were made with impure calcined magnesite, but later, purer materials were obtained. Thus, the first experiment was made with a Grecian calcined magnesite, said to have the following analysis:

SiO_2	0.57
Al_2O_3 and Fe_2O_3	0.45
CaO	4.08
MgO	87.08
CO_2	9.25
	101.43

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After fusion in the electric furnace, we obtained a substance which gave the following analysis:

SiO_2	0.69
Al_2O_3 and Fe_2O_3	1.79
CaO	3.29
MgO	93.68
	99.45

The density of the fused material at 25°, compared with water at 4°, was 3.575.

The densities of specimens of fused magnesia taken from different parts of the same furnace seem to vary greatly. Thus, the densities obtained in the case of four specimens of fused magnesia taken from one furnace were as follows:

Specimen No.	Density
1	3.518
2	3.559
3	3.565
4	3.561

Our investigations have not yet been carried far enough to determine what is the cause of this variation in density. It may, however, be due to the differences in chemical composition. Thus in the case of another furnace analyses of various specimens were made with the following results:

	Specimen No.			
Analysis:	1	2	3	4
SiO_2	1.82	2.50	2.24	2.21
Al_2O_3 and Fe_2O_3	1.76	3.45	2.05	3.20
CaO	1.74	1.10	2.48	1.85
MgO	94.37	92.80	93.63	93.27
	99.69	99.85	100.40	100.53

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In making a study of the physical properties of fused magnesia, it is of great importance that careful analyses be made on the specimens used in the determinations. According to Moissan,[1] the presence of small quantities of impurities greatly lowers the melting point of magnesia, and it is probable that the electrical conductivity is also altered by their presence. Hempel[2] gives 2,250° C. as the melting point of magnesia, or more than 300° higher than Messrs. Goodwin and Mailey, but no analysis of the specimen is given. Perhaps the authors can give us the analyses of the specimens used by them.

As to the chemical properties of fused magnesia, the following experiment may be of some additonal interest. It is well known that the ordinary calcined material slowly absorbs CO_2, forming magnesium carbonate. To determine whether this effect was marked in the case of the fused material, two specimens that had been exposed to the air in the laboratory for six weeks were taken for experiment. Specimen No. 1 was a well-fused material, and was found to contain 0.04 per cent. CO_2. Specimen No. 2 was partially fused or sintered material containing 0.05 per cent. CO_2. Both specimens were placed in porcelain boats and put into a glass tube, through which a current of moist CO_2 was passed for fifty hours. The CO_2 in the specimens was then determined, with the following results:

Specimen No. 1—Per cent. CO_2, 0.42
Specimen No. 2—Per cent. CO_2, 0.63

By fusing magnesia in a specially constructed furnace, it is possible to obtain crystals of magnesia which are apparently produced by sublimation. An excellent photograph of these, kindly made for us by George Curtis, of Niagara Falls, is shown.

[1] Le Four Electrique.
[2] Zeitschrift für Elektrochemie, 22 October, 1903.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, held at Ithaca, N. Y., May 1, 1906, President Bancroft in the Chair.

A NEW SILICIDE OF MOLYBDENUM.

By Oliver P. Watts.

During the last fifty years the preparation of the metallic silicides has been a fruitful field for experimental investigation. In the year 1893 only eleven compounds of silicon, with seven different metals, were known. The application of the electric furnace to this line of research resulted in a great extension of the list of metallic silicides, now thirty-two in number. And the end is not yet.

The existence of a silicide of molybdenum seems to have been first pointed out by H. N. Warren[1], but it was first isolated by Vigouroux[2] in 1899. Its constitution is expressed by the formula Mo_2Si_3. It consists of silver-white prisms of metallic appearance, and is not acted on by any single acid or by aqua regia. The substance was prepared by the reduction of a mixture of the oxides MoO_2 and MoO_3 by 40 per cent. by weight of silicon in a carbon crucible in the electric furnace. The excess of molybdenum in which the silicide was contained was then removed by using the ingot as anode in hydrochloric acid. The crystalline residue resulting from this treatment was further purified by the successive action of aqua regia, caustic potash solution, and hydrofluoric acid, but still contained as impurity a small amount of iron silicide which could not be removed.

In 1904-5 the writer attempted to prepare a series of compounds of the metals with both silicon and boron, *i. e.*, silico-borides. Among other metals employed was molybdenum, and, although the method used, that of the simultaneous reduction in the electric furnace of the oxides of the three elements, proved unsatisfactory for the production of silico-borides, one of these experiments seemed to indicate the possibility of the existence of a higher silicide of molybdenum than that prepared by Vigouroux. This ex-

[1] Chem. News, *78*, 313 (1898).
[2] Comptes rend. *129*, 1238-9.

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periment consisted in heating in the horizontal arc furnace a charge composed of 70 grams "molybdic acid," 30 grams silica, 50 grams boric anhydride, 106 grams copper, and 120 grams aluminum, one-half in the form of powder, with cryolite as a flux and lime as a retarder to prevent too violent a reaction. The charge was placed on a bed of magnesia and heated for 16 minutes by a current of 350 amperes at 70 volts. The resulting ingot was pulverized in an iron mortar, and treated for several days by frequently renewed quantities of nitric acid diluted with an equal volume of water. The residue was then treated by dilute hydrofluoric acid to remove silica, washed by water, alcohol and ether, and dried. The product consisted of aggregations of flat, dark crystals with a metallic lustre. Analysis showed their composition to be,

	Per cent.
Molybdenum	62.4
Silicon	34.2
Iron	1.1
Boron	2.3

Treatment by hot hydrofluoric acid removed some silicon and all the iron present. The residue was unaffected by boiling aqua regia, but was completely soluble in a mixture of hydrofluoric and nitric acids.

Now hydrofluoric acid really dissolves all the silicides of iron, but is without action upon the boride of iron, therefore all the iron was present as silicide; hence the boron is present as molybdenum boride. Iron boride was undoubtedly present in the original ingot, but was destroyed by the treatment by nitric acid. Since crystallization occurred in a large amount of copper there can be no free silicon present. After deducting the silicon required for the iron present as $FeSi_2$, and the molybdenum required by the boron, the residual molybdenum and silicon are far from the proportions required by the formula Mo_2Si_3, but correspond closely with the formula $MoSi_2$.

The action of several reagents upon this substance is as follows:

Boiling nitric acid—no action.

Boiling aqua regia—no action.

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Boiling hydrofluoric acid—no action.

Fused sodium carbonate—action with incandescence.

Fused sodium nitrate—slow, but complete decomposition.

Its specific gravity is 6.31 at 20.5° C.

An earlier experiment, in which a mixture of molybdenite and silica was reduced by calcium carbide, gave a similar result in the ratio of silicon to molybdenum.

While no pure silicide of molybdenum has been isolated in these experiments, the only explanation the writer can offer for the high content in silicon is by the presence of a silicide of molybdenum richer in silicon than Mo_2Si_3, and probably having the formula $MoSi_2$.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, held at Ithaca, N. Y., May 1, 1906, President Bancroft in the Chair.

THE REDUCTION OF METAL SULPHIDES.

By Oliver W. Brown.

The ease and completeness with which zinc sulphide is reduced to metal, when mixed with lime and carbon and heated in an electric furnace, led the writer to believe that this same method might be useful in the reduction of molybdenite. The experiments on the reduction of this mineral, which the writer carried out in 1903, may be of interest to members of this Society.

The sulphide of molybdenum, which is the principal source of this metal, is usually roasted until the sulphur is completely expelled and the impure oxide of molybdenum obtained. This oxide may be purified by the usual chemical methods and then reduced to metal by smelting with carbon in the electric furnace. If only a commercial metal is desired, the impure oxide, obtained by roasting the molybdenite, may be smelted with carbon without being purified. A considerable amount of molybdenum is lost during the roasting process, as the oxide is volatile at the temperature required to expel all of the sulphur.

The reduction of the comparatively non-volatile molybdenite directly to metal would save the cost of roasting, and prevent the loss of molybdenum which takes place during the roasting process. The writer has found that molybdenite is easily and completely reduced to solid metal by electric smelting with lime and carbon.

Guichard[1] claims that he has obtained a crude molybdenum by heating the natural molybdenite in a carbon tube in an electric furnace, and that the metal produced contained no sulphur. Repeated trials by the writer along this line have failed to produce a metal free from sulphur. When molybdenite was heated to a very high temperature in a crucible of Acheson graphite, which was closed with a plug of graphite, a brittle mass high in sulphur and of non-metallic appearance, was obtained. In other experiments molybdenite was heated in open graphite crucibles. Very

[1] Guichard: Compt. rend. *122*, 1270.

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high temperatures were tried, and the best metal that could be produced was badly mixed with slag, and could not be separated from it until it was broken into small fragments and digested for several hours with hot concentrated hydrochloric acid.

An analysis of the purest sample of metal obtained by this method, after being purified by repeated boiling with hydrochloric acid gave,

	Per cent.
Molybdenum[2]	96.60
Carbon	2.58
Iron	0.20
Sulphur	1.37
	100.75

The long boiling of the small fragments of metal with concentrated hydrochloric acid probably very materially reduced the quantity of iron and sulphur in the metal.

The reduction of molybdenum sulphide with lime and carbon gives a well-fused metal containing a very small amount of sulphur. The molybdenite used in the experiments described below contained 36.3 per cent. molybdenum, 28.96 per cent. silica and about 5 per cent. of iron. The molybdenite, lime and carbon were pulverized to pass a 20-mesh sieve. A charge containing 160 grams molybdenite, 120 grams lime and 84 grams of graphite was smelted in a vertical resistance furnace. The constituents of this charge are in proportions represented by the equation

$$MoS_2 + 2CaO + 7\,C = 2CaC_2 + 2CO + CS_2.$$

A 1¼ x 4-inch round carbon resistor was placed vertically in the center of the furnace. This made contact with a round Acheson graphite electrode 1¼ inches in diameter, which entered the furnace from the top, and the graphite lining in the bottom of the furnace. The charge was packed around the 1¼-inch carbon resistor, and a few pieces of coke were laid on top of the charge. A current was passed through the furnace for 1¾ hours. During the first hour a current of 207 amperes at a pressure of 21 volts

[2] The amount of molybdenum in this and other samples of metal referred to in this paper was determined by Frank C. Mathers in the Electrochemical Laboratory of Indiana State University.

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was used. At the end of the first hour the carbon resistor burned out, and the furnace was operated as an arc furnace during the remainder of the run with 300 amperes at 40 volts.

At the beginning of the run a large amount of sulphur dioxide was liberated. This was undoubtedly due to the molybdenite in the top layers of the charge being roasted to oxide. After the current had passed for ten minutes a flame about 6 inches long shot out of the furnace, but soon died down.

After the furnace had cooled it was torn down and the contents removed. About 40 grams of white, hard metal was found in the bottom of the furnace immediately around the lower end of the carbon core. The metal had been well fused, could be easily broken with a hammer, and was not malleable. A layer of porous, crystalline, resin-like material, containing molybdenum, was found immediately above the metal. This substance probably contains a carbide of molybdenum.

A mixture of 160 grams molybdenite, 112 grams lime and 24 grams of graphite was next prepared. The relative quantities of material in this mixture correspond to those in the reaction,

$$MoS2 + 2CaO + 2C = Mo + 2CaS + 2CO.$$

The charge was smelted in the resistance furnace used in the last experiment. The charge was packed in the furnace around a ¼ x 4-inch carbon resistor, and was covered with powdered lime. A current of 275 amperes and 25 volts was passed for 52 minutes. Much lime was blown out of the furnace by the escaping gases. About 40 grams of metallic molybdenum was obtained. No carbide seemed to be present, but quite a large amount of nearly white, well-fused calcium sulphide was removed from the furnace.

Many experiments were carried out with a mixture containing the same relative quantities of lime, carbon and molybdenite as that used in the run just described. Various forms of furnace, different amounts of electrical energy, and heating for different lengths of time were tried, and a good yield of metal was usually obtained. The metal was usually found at the bottom of the furnace, covered by a layer of impure calcium sulphide; however, when the heat was not sufficient, the metal was sometimes scattered through the calcium sulphide in particles the size of shot. The calcium sulphide from the different runs was tested for

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molybdenum, but in no case was a trace of the metal found, showing that the reduction to metal is complete. In one experiment a charge of the same composition as that last described, was placed in a magnesia-lined Acheson graphite crucible and heated in a Moisean arc furnace of limestone for 43 minutes, with a current of 200 amperes at 55 volts. After the furnace had cooled, a well-fused button of metallic molybdenum, weighing nearly 50 grams, was taken from the crucible. The temperature had been so great that nearly all of the calcium sulphide was volatilized from the furnace, leaving the button of metal almost bare. An analysis of this metal gave,

	Per cent.
Molybdenum	93.80
Iron	5.51
Carbon	0.87
Sulphur	0.032

The analysis of an ingot of molybdenum obtained by fusing together the metal obtained from several experiments gave the following:

	Per cent.
Molybdenum	97.41
Iron	1.50
Carbon	1.51
Sulphur	0.05

The refusion of the metal seems to rid it of a large part of the iron, probably by volatilization.

The largest amount of sulphur which was found in any of the samples of molybdenum, made by smelting with lime and carbon, was 0.25 per cent.

The foregoing experiments show that a complete reduction of molybdenite to metal takes place when it is smelted with lime and coke. An excess of lime in the charge seems to be of advantage, while an excess of carbon leads to the formation of carbide which holds back some of the molybdenum. This method of reduction is superior to the ordinary roasting to oxide and subsequent reduction with carbon in that it prevents loss of metal by volatilization of the oxide and also entirely dispenses with the roasting process.

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Experiments were next tried on the reduction of the sulphides of lead, copper, iron and nickel.

When galena was reduced in the electric furnace with lime and coke, very little metallic lead was obtained. The incomplete reduction of the lead sulphide is probably due to the formation of a stable double sulphide of lead and calcium, according to the reaction represented by the equation[3]

$$2PbS + CaO + C = Pb + PbS.CaS + CO.$$

Impure metal was obtained when sulphides of either copper, nickel or iron were smelted with lime and coke; however, the results did not encourage further experimental work, as it does not seem that the reduction of these metals in this manner would be of commercial value, even if a fairly pure metal were produced.

As metallic antimony boils at the comparatively low temperature of 1,100° to 1,400° C., it appears that its sulphide ore could be reduced to metal and distilled in a manner analogous to that which may be used with zinc blende.[4] Some experiments were carried out with mixtures of stibnite, lime and coke. The materials were pulverized until they passed a 20-mesh sieve. The stibnite contained 47.65 per cent. of metallic antimony. Charge No. 1 contained 168 grams of stibnite, 84 of lime, and 118 grams of coke. The relative weights of these materials correspond to the equation,

$$(1)\ Sb_2S_3 + 3CaO + 3C = 2Sb + 3CaS + 3CO.$$

Charge No. 2 contained stibnite 168 grams, lime 42 grams, and coke 36 grams, and corresponds to the equation,

$$(2)\ 2Sb_2S_3 + 3CaO + 12C = 4Sb + 3CaC_2 + 3CS_2 + 3CO.$$

The mixtures were placed in assay crucibles which were loosely covered, and then heated for one hour in a hot coke fire in a wind furnace. After removing the crucibles from the fire small globules of metallic antimony were found, scattered through charge No. 1. Five or six grams of metallic antimony possessing the characteristic color and fracture were found near the bottom of the crucible containing charge No. 2.

Several attempts were made to obtain metallic antimony by heating mixtures of stibnite, lime and coke in an open electric

[3] Handbook of Metallurgy, Schnabel *1*, 341.

[4] Brown and Oesterle, Trans. Am. Electrochem. Soc., *8*, 171.

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furnace. The furnace, whose interior dimensions were about 3 inches square by 4 inches deep, was lined with Acheson graphite plates. The graphite lining served as one electrode, and a round carbon rod 1¼ inches in diameter, which was suspended in the furnace, served as the positive electrode. Mixtures corresponding to equations Nos. 1 and 2, given above, were heated with currents of about 150 amperes and 25 volts. In these experiments the upper electrode was generally lowered until it touched the bottom of the graphite box, and the charge was then poured in around the electrode. On slightly raising the upper electrode an arc was easily started, which, at the commencement of the experiment, was completely covered by the charge.

In all experiments in which an open electric furnace was used for heating either of the above charges, much antimony oxide volatilized, and only a very little metal was found scattered through the charge in small beads.

Experiments were next carried out in an enclosed electric furnace. This furnace was made by fitting an air-tight cover on the furnace, used in the experiments described above. The cover was insulated from the body of the furnace by a layer of asbestos cloth about ½ inch thick. The carbon anode entered the furnace through a sleeve in the cover. The sleeve was provided with a packing of asbestos cord, to insure that the joint between it and the carbon electrode would be gas tight. A 1½-inch iron pipe, about 8 inches long, was inserted in one side of the furnace, and served as a condenser for the antimony which distilled from the furnace. During the smelting of the charge the outer end of the tube was almost completely closed with a fire clay plug.

In one experiment a charge containing 168 grams stibnite, 42 grams lime and 36 grams of coke, was smelted. The upper electrode was first placed in the furnace, with its lower end resting on the bottom. The charge was poured into the furnace around the electrode, and the cover was then placed in position. Several bricks were placed on the cover, to press it down firmly and render the furnace practically gas tight. On starting the current the carbon electrode was slightly raised, in order that an arc would form between the upper electrode and the graphite lining of the furnace. A current of 169 amperes and 27 volts was passed through the furnace for 40 minutes. Very little oxide escaped. Pieces of

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metallic antimony as large as peas condensed on the walls of the furnace. The heat was not great enough to distil much of the metal into the condenser. Twenty-three grams of metallic antimony were collected, but many small beads of metal, which remained in the charge, could not be saved. Some antimony powder, mixed with oxide, was removed from the condenser. The charge remaining in the furnace after the run contained much sulphur, but no calcium carbide.

As the temperature in the experiment just described was not high enough to cause all of the metal which was reduced to distil from the furnace, another experiment was tried on a charge of the same composition and under the same conditions, except that a current of 190 amperes and 35 volts was passed through the furnace for one hour and fifteen minutes. Much antimony burned up in this experiment. During the run the iron case which enclosed the furnace was red hot, yet the charge remaining in the furnace contained 23.16 per cent. of antimony.

A charge containing 336 grams of stibnite, 168 grams of lime, and 36 grams of coke, was next heated in the furnace. As is seen, this charge contains the relative amounts of lime, coke and stibnite required by the equation,

$$Sb_2S_3 + 3CaO + 3C = 2Sb + 3CaS + 3CO.$$

A current of 181 amperes and 28 volts was passed for one hour. Much metal distilled, about 12 grams condensing as solid metal and some as powder, while a larger quantity escaped and burned up. A flame 7 inches long burned from the mouth of the condenser during part of the run. The slag remaining in the furnace contained 8.34 per cent. of antimony.

These experiments seem to show that the reduction and distillation of antimony from a charge of stibnite, lime and carbon is incomplete, even when the mixture is heated in an electric furnace to a very high temperature.

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DISCUSSION.

MR. CARL HERING: I would like to ask Prof. Burgess what the efficiency was in the reduction of molybdenite; that is, whether there was considerable molybdenum lost in that reduction. Molybdenite is a rather expensive ore, I think it is worth 50c and 60c a pound; therefore in commercial reductions it ought not to be lost in large quantities.

PROF. BURGESS: I don't think Mr. Brown has given the actual figures which demonstrate that; he says, however, that in the residue which was in the furnace (the slag) there was no trace of molybdenum. The only way the molybdenite could have been lost, therefore, would be by volatilization and if it had volatilized to any appreciable extent, he would have detected it by its condensing around the furnace electrodes and surrounding parts; so I think he gets a nearly complete utilization of his molybdenite. The figures which he gets for the power consumption cannot be taken as giving what would be obtained in practice, since he used such a small furnace.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, held at Ithaca, N. Y., May 1, 1906, President Bancroft in the Chair.

CATHODIC DISINTEGRATION OF CARBON IN ELECTROLYTE OF FUSED SODIUM CHLORIDE.

By George I. Kemmerer.

The fact that graphite is unattacked, and that other forms of carbon are fairly durable when used as the anode material for the electrolysis of fused sodium chloride, is well known. It does not appear to be so generally known that the same material when used as the cathode is rapidly consumed. Professor C. F. Burgess observed in connection with certain investigations on fused chlorides some years ago that carbon and graphite are among the most undesirable materials which can be used for the cathode, and he suggested to the writer that some notes on further observation of this phenomenon might be of interest.

Accordingly, trials were made which showed the relative amount of disintegration which was suffered by carbon rods, such as are ordinarily used in electric arc lamps and similar material which had been graphetized by the Acheson process. Preliminary experiments showed that the carbon rods were very rapidly disintegrated, making it necessary to feed them continually into the electrolyte, as the lower portion was corroded away. While appreciable corrosion was detected on the Acheson graphite, it was less than 1 per cent. of that which occurred on the carbon. In conducting the quantitative trials the electrolyte was first fused, employing a graphite cathode which, when a suitable temperature was obtained, was quickly replaced by a weighed rod of carbon or graphite ⅜ inch square, and dipping 1½ inches below the surface of the electrolyte. A current of 27 amperes was employed, the pressure required being 24v. with the graphite cathode, and 27v. with the carbon. This difference of pressure was probably accounted for by the difference in specific resistance of the materials. After the passage of the current for a measured interval, the rods were well washed, dried at 100° C. and again weighed. The following data was thus obtained:

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Graphite Cathode—
Current 27 amperes—24 volts.
Time, 10 minutes.

Weight before	29.792	grams
Weight after	29.658	
Loss	.134	

Carbon Cathode—
Current 27 amperes—24 volts.
Time, 1½ minutes.

Weight before	39.215	grams
Weight after	32.48	
Loss	6.735	

The experiment with the carbon rods was repeated several times, various samples of carbon being employed, but in each case the portion dipping into the electrolyte was completely disintegrated in from 1½ to 2 minutes.

In weighing the graphite rods subsequent to electrolyzing and after washing with water for 10 minutes and drying at 100°, it was found that both samples had gained in weight, but this was found to be due to the fact that the salt had not been completely dissolved out. It was found then that after washing for two days and drying at 100°, the losses given in the above data were obtained.

This marked cathodic disintegration seems to be somewhat analogous to that phenomenon which Mr. C. J. Reed discovered with lead when used in certain aqueous solutions, and employing a high current density.[1] In just what manner the cathode product causes the disintegration is perhaps not so evident. The most natural supposition is that the liberated sodium unites chemically with the carbon forming a sodium carbide. To test whether this might be the case the electrolyte was allowed to cool after electrolysis had proceeded for some time and the solidified mass was treated with water, but no gas was evolved, as might have been expected had

[1] Journal Franklin Institute, 1895.

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sodium carbide been present. Moissan[2] has shown that sodium carbide is decomposed if heated to redness, and this being the case the sodium carbide, should it be formed at the cathode, would be immediately decomposed at the temperature of 815° C., at which it is necessary to maintain the salt in order to keep it molten. The carbon which remains after dissolving the salt settles to the bottom as a coarse, black precipitate, which is undoubtedly amorphous carbon.

It was found that the amount of disintegration was not proportional to the quantity of current, as would be indicated by the application of Faraday's laws, but that current density and temperature seemed to exert an influence. It is evident that inasmuch as the carbon corrodes at a rate greater than that calculated from its electrochemical equivalent, there must be a physical as well as chemical disintegration of the material.

Applied Electrochemistry Laboratory,
University of Wisconsin.

DISCUSSION.

PRESIDENT BANCROFT: I don't quite understand what the connection is between Faraday's law and the cathode corrosion; because it seems to me that the disintegrating action between lead and sodium hydroxide depends on the formation of an alloy which afterwards breaks down, and there is no conceivable way of predicating what the composition of that alloy would be—therefore what the amount of corrosion of lead would be for a given current.

PROF. BURGESS: The suggestion is made that the reason carbon is disintegrated is that the sodium liberated upon the surface forms a sodium carbide. This carbide decomposes, however, at this temperature. From electrochemical equivalents we calculate that with a certain current we get a certain amount of sodium liberated; and if that sodium would form a carbide, we would be able to calculate how much carbon would be removed in that reaction; but the amount is much greater than such a calculation would give us.

[2] The Electric Furnace, p. 204, Lenher's Translation.

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PRESIDENT BANCROFT: If you assume that the disintegration is due to the formation of a definite compound breaking down, then that is strictly true. If a solid solution were formed, or if there were absorption, there would be no relation between Faraday's law and the amount of corrosion.

DR. FORSSELL: I would like to call attention to the known fact that ordinary carbons are not composed of elementary carbon only, but consist also of high-molecular compounds of carbon with hydrogen and perhaps other elements. These will manifest themselves sometimes in otherwise inexplicable chemical reactions. For instance when a certain grade of carbon was treated for a long time with an ammoniacal cupric-chloride solution, the carbon disintegrated considerably. We have also found in a special case that there existed several times more sulphur in a carbon than could be accounted for, if it is assumed that the metallic impurities occurred as sulphides. This fact tends to prove that the sulphur occurred in some compound with carbon and possibly hydrogen. Under these circumstances the violent action on carbon cathodes, referred to in this paper, seems a little more easy to explain.

MR. HUGH RODMAN: In some aqueous solutions coke disintegrates as cathode while graphite remains intact. Is there no reason to believe this disintegration due to a binder or impurity in the coke?

PRESIDENT BANCROFT: Isn't that largely a question of porosity in the two cases?

MR. RODMAN: I do not see why the porosity should affect its disintegration; perhaps because it is structurally weak?

PRESIDENT BANCROFT: Yes, and possibly because there is an evolution of something which occupies a larger volume.

MR. RODMAN: Being porous it should have a larger surface and not be as liable to destruction by gassing.

MR. CARL HERING: In what form does this lost carbon reappear?

DR. FORSSELL: I do not believe that the phenomenon discussed is analogous to the disintegration of lead cathodes. The occurrence of the black precipitate more likely is due to the structure of the carbon electrode. It is generally known that ordinary carbons consist of carbon-flour, cemented together with a car-

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boniferous binder. When the green carbon is being baked, the binder naturally will shrink most, the remaining material thus becoming more porous than the flour. If the baked carbon is exposed to the action of some reagent, the binder will be more readily destroyed or consumed, leaving the flour behind. It is evidently this flour that appears as a black precipitale in this case. The same kind of action frequently occurs in electric furnaces when air has slight access to red-hot carbon terminals. On such places they will be covered with a soft mass of carbon, consisting of the flour, the binder having burnt away.

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SODIUM PRODUCTION; A NEW PROCESS.

By Edgar A. Ashcroft.

Part I.—Commercial.

The modern industry of sodium production which, with its very profitable derivatives of peroxide and cyanides, has been the honorable and well-merited increment and outcome of the earlier work of the late Mr. Hamilton Young Castner, and the energetic and capable business men who adopted and applied his inventions, has reached, in the present day, quite considerable dimensions.

Such statistics as are available show that the production of the metal, in the United States alone, is approximately 1,200 tons per annum; whilst in England, and also in Germany, nearly similar amounts are produced.

The disposal of this considerable quantity of a metal which most of us can remember as almost a rarity—(its price I think used to be about ten shillings an ounce when procured for some of my youthful experiments)—takes place somewhere about as follows:

Used for cyanide making.....	1,500	tons
Used for peroxide making.....	1,500	"
Sold as metal.....	500	"
Total of world's production.....	3,500	"

The figures of course are only approximate.

The price of the metal has gradually fallen during the last few years from sixty cents a pound or thereabouts to some twenty-five cents a pound which is about the price to-day for large steady contracts.

Every one acquainted with the current practice of electrochem-

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istry is familiar with this important and successful process; and its application at Niagara Falls has been described before this Society. Many competitors have arisen, and particularly, many attempts have been made to produce the metal by direct electrolysis of salt; but it is safe to say that none of these have, as yet, attained any substantial success; and, now that the older and successful process is becoming public property, through the expiry of patents, still less encouragement will be offered to possible competition in the future.

In spite of these handicaps the author, like most inventors, having a discursive kind of muse, has strayed into this field, and is now asking your kind attention to a brief account of a new method of production. I have long felt that a genuine field for improvement exists in this growing industry, and my reasons are briefly as follows:—

Practically all the sodium at present made in the world is made by the Castner process which, as you well know, consists in electrolysing a pure form of caustic soda between electrodes of iron and nickel. Therefore, for the purpose of this commercial view of the subject, we may dismiss all others from the consideration.

The costs of this process are known, and are broadly as follows, per pound of sodium produced:—

Caustic soda.....	$ .05
Power according to locality.....	.01 to .05
Labor	.025
Upkeep and standing charges.....	.02

(I believe the power at Niagara Falls would work out at about .025 and at Runcorn (England) where gas engines and steam engines are employed at about .035 to .04) making a minimum possibility of cost under existing conditions of from 10.5 to 14.5 cents per pound. There are no by-products. As the metal commands a high price and the derived products a still higher price, and as the market during the past few years has been steadily growing, it is to be presumed that the manufacture has been highly profitable. Until last year this process was protected in England by the Castner patent, now expired.

The new process makes the metal by electrolysing common salt in a fused state. This is made possible by the invention

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which I shall presently describe, and which consists in electrolysing in a double electrolysing apparatus, receiving the sodium in the first cell into alloy with molten lead, transferring this alloy to a second cell when it is used as an anode, and causing the sodium to be recovered in an electrolyte (such as caustic soda) which is not consumed.

The process is very simple and inexpensive. The cost when working on the same scale as the above estimate for the Castner process will be as follows:

Common salt.....	$ .005
Power according to locality.....	.01 to .05
Labor	.01
Upkeep and standing charges.....	.025

Making a gross cost of 5 cents to 9 cents per pound of sodium produced, according to the cost of power.

In addition to this very substantial reduction in cost of manufacture, the new process produces a by-product of pure chlorine gas which may be worked up by well-known methods into any of the numerous chlorine products, notably, zinc chloride, bleaching powder, potassium chlorate, stannous chloride, sulphur chloride, carbon tetra-chloride or chloroform.

The value of this (if worked up into the heavier products like bleaching powder) is approximately 2¼ cents per pound of sodium (net after deducting cost of working up the bleaching powder). The value would be considerably greater if worked up into some of the products named; but as this condition applies practically the same to all chlorine and alkali processes it forms no special feature of the present case and therefore I do not dwell upon it.

It will be seen that the power factor in each of the above two cases is practically identical, the Castner process requiring 4½ total volts per cell and yielding 45 per cent. real current efficiency, whilst the author's process requires 9 volts (7 and 2) per double cell, but yields twice the amount of metal (or 90 per cent. real C. eff.) for a given current.[1]

[1] The low current efficiency of the Castner process (a point by the way which has been often misstated) in comparison to the author's method (both delivering the sodium from caustic soda) is due to the chemical necessity which exists in Castner's method for decomposing an equivalent of water for every equivalent of sodium set free from caustic; a necessity which does not exist under the peculiar conditions of the electrolysis of caustic in the Ashcroft arrangement, as may be seen by a study of the reactions.

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Under these circumstances it will be seen that the commercial conditions (as to locality of works, etc.) for the two processes are practically identical and great advantages are claimable, by this industry for "cheap power" sites.

The following table shows the comparative cost of the several known means of producing power for such processes:—

	Steam Engine Average	Gas Engine Average	Oil Engine Average	Niagara (Water) Average	Norwegian (Water) Actual
Cost of fuel, Labor and upkeep, Capital charges,	$40.00	$30.00	$15.00 2.75 7.25	$20.00	0 $2.50 5.00
	$40.00	$30.00	$25.00	$20.00	$7.50

Certain Norwegian water sites thus produce electrical energy cheaper than any other form of production in the world.

Applying these figures of power to the manufacture of sodium, the result is approximately as follows per ton of metal produced:—

Steam	Gas	Oil	Water Niagara	Water Norway
$120.00	$90.00	$75.00	$60.00	$22.50

Indicating at once the enormous advantage of working at the "cheapest power" sites, an advantage which will be felt more and more should the price of the metal decline with large productions in future years.

But the question of transport is also important to the commercial issues, and the site of the works should be chosen with this also in view.

The metal is at present transported in packages of 200 pounds weight. The package consists of a sealed metal drum into which the sodium is packed in 5-pound cakes, taken direct from the producing plant. The peroxide is packed in 10-pound tins, placed inside a wooden box. The cyanide is also exported in sealed packages. The packages are returnable (except from very long distances) and in actual practice are found to last well,

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so that the entire cost of packing and transport has been now brought to a very low figure.

No special precautions are necessary beyond the exclusion of air and water. Although a few years ago sodium and its products would have been regarded as dangerous chemicals for transport purposes, the experience of the last few years has removed nearly all restrictions, and cheap freights now prevail in most countries. I believe the rates of carriage in this country moreover are sufficiently low to minimize the economical necessity which exists in most other lands, for getting right on the seaboards with all such factories.

I will conclude this section of the paper by a brief statement of some of the special reasons which lead me to hope for a large extension of the sodium industry in the future.

(a) The metal is produced from an ore (common salt) which can be obtained everywhere at a low cost as compared to any other metallic ores, and which contains no less than 40 per cent. of the metal with scarcely any impurities or other contents except the combined chlorine (60 per cent.). These conditions are unique and ideal from the metallurgist's point of view.

(b) The metal can be produced by the new process with an expenditure of no kind of material at all, except the salt (this corresponds to the ore in other metallurgical operations), and a trifling amount of incidental stores. When producing on a large scale, almost the entire cost of production will be for electrical energy and, given "cheap power" conditions, the cost of production by the new process may ultimately be brought very low indeed. These conditions are unique and ideal from the purely commercial point of view.

Thus there seems no reason why sodium when produced on a very large scale by the process which I have the honor to describe to you, under favorable conditions as to power, etc., should not, some day, be sold as cheaply for instance as iron or steel. When such a state of the industry occurs it is extremely probable that greatly extended uses will be found for the metal, for very special physical, chemical and electrical properties also attach to this metal; properties which in fact are quite unique, thus:—

1. It is the lightest of all common metals, not excepting aluminum.

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2. Its chemical properties are unique. It decomposes water freely by mere contact, producing a large volume of hydrogen gas and a by-product of caustic soda. This property suggests at once the use of water and sodium as balloon ballast for long journeys so that when the ballast was to be discharged a simultaneous refreshment of the gas could be secured as well. It has the greatest energy of combination, weight for weight, with chlorine, oxygen, etc., of all the metals (excepting aluminum which is an inherently much more expensive metal owing to the prevailing impurity of its ores and the difficulties of its reduction), and on this property reasonable hopes are founded that it will some day find extensive application as a medium (either secondary or primary) for batteries having the object of producing or conveying to a distance cheap electric energy. It reduces most oxides or salts of other metals, setting free the metal, and it is reasonable to suppose that this property may insure its finding further extensive employment in metallurgical industries (particularly iron and steel production, and purification; or in the chemical reduction of sulphide ores in remote localities) when it shall be produced in large quantities at prices that will satisfy economical conditions.

3. It has, weight for weight, the greatest electrical conductivity of all the metals. On account of this property it is rather confidently expected by some people that the metal will shortly find application as a substitute for the more expensive metal, copper, as a conductor for heavy currents of electricity.

4. It is the softest and most malleable of all metals and it melts at 90° C, or below the boiling point of water. It is therefore easily triturated and mixed for use with any reaction materials.

5. But by far the largest immediate potential market which exists at the present date for the metal sodium lies in the already extensive and rapidly growing gold-cyanide industry. Before the war in South Africa some 10,000 tons of cyanide were used, yearly, in gold extraction, and since the resumption of operations there, and with steadily extending growth of this form of gold extraction throughout the world it is estimated that the world's consumption of cyanide has reached considerably larger figures; probobly some 25,000 tons per year or more. Although much of this cyanide is manufactured by processes not employing metallic sodium as a base, it is well known that by far the best processes

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in use do so. Only the high ruling prices of metallic sodium have limited the extension of these processes to the exclusion of all others, and a careful comparison of all known costs, shows that whilst cyanide finds a ready market to-day at 16 and 18 cents per pound, but little profit remains to makers at this figure. The sodium employed being valued at 25 cents per pound nearly all the profit is then on the sodium.

As an outlet for cheaper sodium, however, this case is very different. The conversion of metallic sodium into cyanide is possible in several different ways and is a cheap operation. For a works able and willing to market the metal at say 12 cents per pound, effective competition can be instituted with any existing process of cyanide manufacture.

At such a price, with the new method of production, a very handsome profit still remains, whereas with the older methods there is presumably no profit at all.

PART II—TECHNICAL DESCRIPTION.

The process which I shall now briefly describe to you has not yet been commercially applied. The patents were acquired in the early stages of the invention by the United Alkali Co. of Liverpool, and the process has been worked out in detail first by the author, and then by the staff of this company at their central laboratory at Widnes. I regret that I am not authorized to disclose the detailed results of this work, therefore must confine myself here to matters of a more public nature.

The following figures, together with the following description are abstracted from one of the recent and as yet unpublished patent specifications and sufficiently describe the process.

The apparatus illustrated in the drawings, Figure 1 to 7, comprises a composite cell (arranged for the production of the metal sodium from common salt), the two components of which are united by means of a regenerator or heat equalizing device. The system illustrated is of a size suitable for a current of 2,000 amperes or thereabout.

Salt is charged into a hopper A and fuses in the bath at B, (or the salt may be previously fused when convenient).

The main current before passing into positive electrode C from

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Fig. 1.

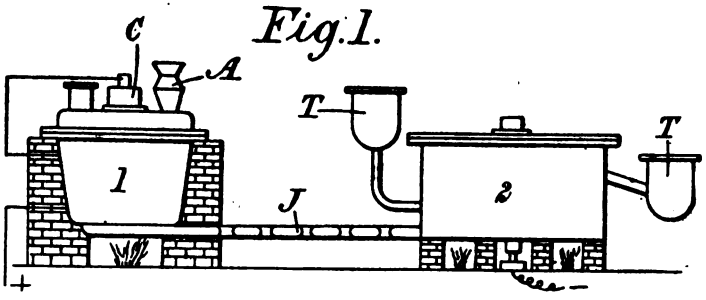
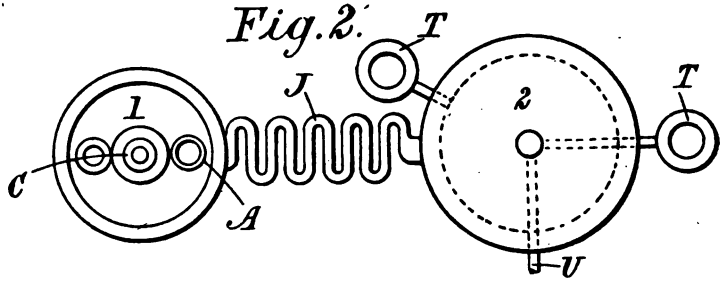


Fig. 2.



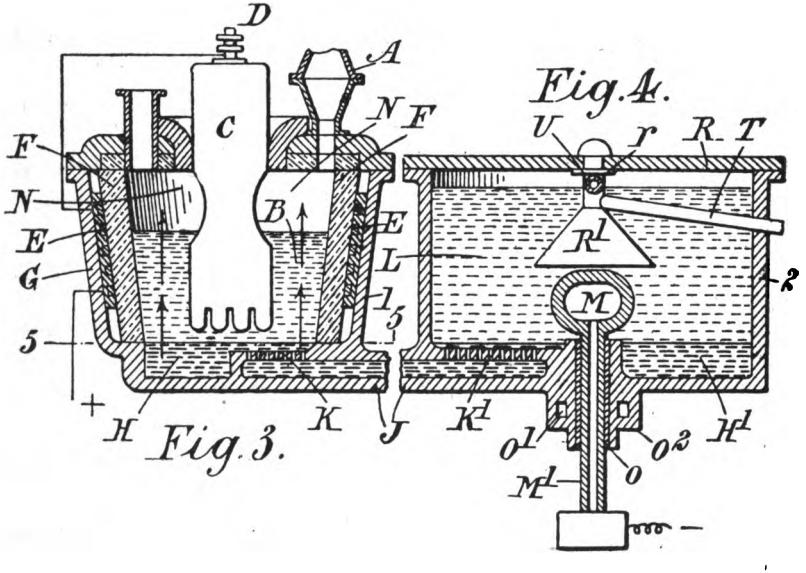


Fig. 4.

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the terminal, makes several circuits around the coil of conductor E placed behind the lining F in the interior of the decomposing cell 1 and thus sets up a strong magnetic field in the iron casing C, the lines of force tending to pass, as shown by the arrows Figure 3. The current crosses the electrolyte, decomposes the salt and then diffuses radially into the alloy, H, of sodium with lead forming the cathode on the bottom of the cell. The radial lines of current in the alloy cutting the lines of magnetic force nearly at right angles cause a motion of the metal in the plane at right angles. The direction of motion of the alloy is indicated by the arrows, Figure 5. The effect of this is to maintain the liquid cathode and the electrolyte in circular motion and as the rich alloy is formed immediately under the carbon anode, it is withdrawn

Fig. 5.

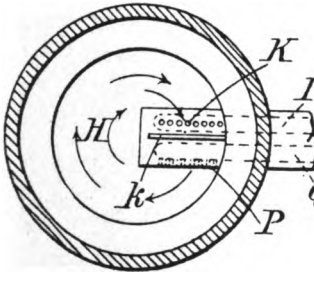


Fig. 6.

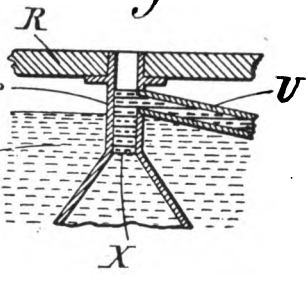
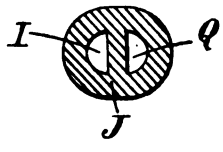


Fig. 7.



from contact with the electrolyte by a skimming action on the surface of the lead, and passes into the division, 1, of the composite pipe, J, through the holes, K, the action being assisted if desired by small baffles, k, (Figure 5).

The adjustment of the magnetic exciting effect of the coil may be accomplished by varying the number of turns of the coil included in the main circuit and for this purpose the several turns of the coil may be connected to a commutator or the like. The main current after entering the fused alloy (acting as cathode) in the decomposing cell, 1, passes along the metal pipes, J, through the alloy (the pipe being preferably arranged, as illustrated, in zigzag form to secure large surface) to the second (or sodium producing) cell 2. Here the alloy acts as the anode, H, and the current traversing the electrolyte, L, (of caustic soda or the like)

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enters the cathode, M, which is preferably of metallic nickel and of globular form, and is connected to a stem, M, of copper, preferably in tubular form, which passes through the bottom of the cell and serves to convey the current out of the bath.

This cathode is insulated from the cell at O, by an insulating sleeve (which may conveniently be composed of the chilled electrolyte) and through its tubular supporting stem a slight cooling effect may be obtained by air circulation (which can be further increased, at will, by circulating any suitable cooling liquid). This has the effect, both of aiding in solidifying the insulation in the sleeve, O, and also slightly lowering the temperature of the bath at the actual point where the sodium is deposited and thus minimising any reaction between the caustic soda and the sodium.

A similar device, to that described for the number 1 cell, consisting of small holes, K, Figure 4, leading out of the composite pipe and backed if desired, by similar small baffles ensures the delivery of the rich alloy at the surface of the bath of molten metal in this cell, and thus in the most active region for the desired removal of the sodium therefrom and causes the alloy to circulate gently in the cell also. After circulating in this cell the depleted lead, now more or less freed from sodium, is withdrawn by the motion of the metal into fine holes placed in the side of division, O, of the composite pipe, J; thence it passes along the pipe and returns through similarly arranged small holes, P, (see Figure 5) laterally into the decomposing or salt cell, thus completing the circulation.

The working temperature of the metal in the salt (or decomposing) cell, is approximately 700 degrees, C, when ordinary commercial salt is being decomposed. Other electrolytes which I can use with this process and apparatus, such as sodium sulphide, sodium carbonate, sodium nitrate, potassium chloride, sodium or potassium iodide, bromide, etc., or mixtures of the same, mostly require a lower temperature. The temperature in the second (or producing) cell is determined by the secondary electrolyte in use.

It is requisite for the successful production of sodium when caustic soda is employed as electrolyte in this cell to maintain the temperature very close to 330 degrees, C, but when other secondary electrolytes are used, this temperature is modified to suit. By means of the regenerative device shown, the alloy passing through the composite pipe, J, in opposite directions in the two divisions,

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transfers heat and thus tends continually to equalize the temperature of the adjacent passages at both ends. By this means, the hot alloy leaving number 1 (or decomposing) cell, heats the cold alloy arriving from the number 2 (or producing) cell and the cold alloy leaving the number 2 cell, cools the too hot alloy arriving from the number 1 cell, so that the desired temperature is maintained in both cells without waste of heat.

For the purpose of collecting the sodium deposited on the globular cathode, M, in number 2 cell, the cell is preferably sealed from the air by cover, R, and a funnel-shaped nickel screen, R, terminating in a small pipe, r, of restricted sectional area is affixed to, and remains, preferably, in electrical contact with the cover, R, and thus with the entire anode system of the cell. The effect of this somewhat unusual arrangement is to preclude the possibility of sodium being set free in any part of the cell, except on the isolated globular cathode, from which it is immediately disengaged by gravity; and, any sodium re-dissolved by anode action at the point, X, will react with the caustic according to the normal reaction, 2Na OH (subjected to current) $=$ 2Na (cathode) $+ H_2O + O$, and $2Na + H_2O + O = 2$ Na O H, again and not according to any of the reactions (such as $2Na +$ 2Na O H $= Na_4O + H_2O$ or 2Na O H $+$ 2Na $= 2Na_2O + H^2$) which are found to take place when sodium metal remains long in contact with caustic soda. Sodium is thus again set free at the cathode and normal caustic reformed at the anode, so that any *leak-current* has no detrimental effect on the composition of the electrolyte, and furthermore prevents direct chemical action.

All the metal set free on the cathode, as already stated, immediately floats by gravitation to the surface and enters the restricted pipe, r. Being lighter than the caustic electrolyte, its level rises and it can thus be caused to leave the cell continuously, as fast as formed, and collect in a suitable bath or receptable by passing along a suitably placed pipe, U, (Figures 4 and 6). The restricted area of contact between the sodium and the caustic ensures that any possible corrosive action on the deposited sodium is reduced to a minimum, and the total efficiency of the cell thus increased to a maximum. The precise form of the above improvements relates to the fact that it has been found that the action of the sodium on caustic, when long exposed tends to form oxides and

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sub-oxides which reduce the efficiency of the caustic as an electrolyte. It may, therefore, sometimes be desirable to periodically renew the caustic by circulating it through the pipes and reservoirs, T. The caustic which has been long used in the cell and become inefficient, owing to solution of sub-oxides, etc., can be regenerated and brought into a useful condition again by merely exposing it to the air and allowing it to absorb water, or by treating it with steam, or by cooling and dissolving it in water and re-fusing.

The lining of the first (or decomposing) cell is of any desired material such as magnesia bricks, which are found to withstand well the action of the electrolyte, alloys and other products, but even siliceous or aluminous bricks (which are cheaper) are mostly found to be sufficiently durable. The heat of the cell may be supplied either from within (by the current) or from without by means of the gas jets or fire shown, or both expedients may be resorted to. The second (or producing) cell, when caustic is employed, may be conveniently regulated in temperature by a small supplementary gas flame, which can be adjusted at will. The rigid exclusion of air from the melted sodium is not so necessary when caustic soda is employed, as secondary electrolyte, as it is with electrolytes fusing at higher temperatures, but it is nevertheless desirable to exclude air from the apparatus as much as possible.

It will be clear that a great variety of raw materials and electrolytes may be used with this process and apparatus and that the precise form of the apparatus may be considerably modified for adaptation to each specific use without departing from the spirit of this invention. For instance, salt may be used in both cells. Carbonate of soda or sodium sulphide, nitrate or nitrite, or mixture of these with sodium chloride or other medium, may be used in the first cell as raw material and the anode material suitably changed or the caustic electrolyte of number 2 cell may be replaced by sodium bromide or iodide, or mixtures of the same.

It only remains to add that simple and small as the improvements proper to this process may appear; it nevertheless hits off some of the real necessities of the case accurately. Everyone is familiar with the many attempts which have been made to procure sodium by the direct electrolysis of sodium chloride.

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Only those who have tried it, however, not on paper, but in factory scale experiments, know how difficult a problem it is. In the first place salt fuses at about 780 degrees C, and sodium vaporises at nearly the same temperature. Therefore, such processes must collect two gaseous products, chlorine and metal, and the apparatus must be arranged so as to keep them religiously apart. But at this and even at much higher temperatures the vaporisation of the sodium is far more rapid or complete. It floats about in great blobs on the surface and eagerly seeks every opportunity of meeting with its beloved chlorine. The real practical difficulty of avoiding all this, and of simultaneously excluding all air is enormous.

As far as I know, these and other difficulties of a practical nature have never been effectually surmounted in spite of many paper processes and many immature patents; it would be rash however, to predict that they never will. As sodium chloride is a true electrolyte and one which does not (the sub-chloride theory at one time advanced, has been exploded) react with metallic sodium detrimentally, to any great extent, the tendency to work in this direction will probably continue. The nearest thing to success in the direction of electrolysing salt was found in the work begun by Rogers, of Milwaukee, many years ago, and perfected by Acker recently for another purpose. I mean the manufacture of lead sodium alloys direct from salt. The Acker process has been fully described before this Society and has many points in common with the first half of the above described sodium process. But it does not go far enough for the production of metallic sodium.

Here the difficulty of practically dissociating sodium chloride just disappears, for the sodium does not distil from the lead alloy at the melting point of salt; although it begins to distil at a point very slightly higher, and for that reason the temperature and other conditions require very careful adjustment. The process I have described takes full advantage of the work of Rogers, Acker and other workers in the same field, and acknowledgments are due to these. Another fortunate circumstance for this process is the lowering of the fusing point of lead by the just necessary 50 degrees or so, which a slight alloy of sodium brings about, thus enabling the fluid alloy to be used in the second cell without overheating the caustic soda. As caustic soda appears

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to be the one electrolyte from which sodium can be quite comfortably collected in fluid form even whilst exposed to the air, and as it is moreover essentially cheap, there is a decided practical advantage in using this material for the unchanged secondary electrolyte, in preference to any of the other possible salts of sodium which might be employed.

A further point of incidental advantage gained in the sodium end of this process is the avoidance of any liberation of hydrogen. Not only is the current efficiency thereby doubled but the continous, automatic, collection of the sodium is rendered possible, owing to the absence of the continual fusilade of popping hydrogen explosions, which is inseparable from the Castner process.

This circumstance (as well as the cheaper raw material) brings about a substantial reduction in the cost of working.

There are many different ways in which the process may be viewed. Thus if viewed in its relation to the electrolysis of caustic soda only, its advantages are immense, for not only is the efficiency (as against electrolysis with insoluble anode) doubled but the voltage is also reduced by less than half. The only voltage required, in fact is a theoretical voltage of less than 1 volt corresponding to the heat of decomposition of sodium lead alloy and a slight practical excess necessary to keep the caustic fused. In actual practice altogether less than 2 volts.

The proper way, however, to regard the process is as a whole, and regarded thus the advantages lie in,—

1. Cheap raw material,

2. Reduced labor charges, and against these advantages there will be a slightly increased upkeep account.

The reactions which take place under various conditions in the electrolysis of caustic soda are extremely interesting and very complicated, and I should like to devote some space to the consideration of a few of them, but as this paper has already exceeded the length I intended for it, and moreover, as I am given to understand that there will be another paper on that subject before you, I will now conclude by thanking you for the patience with which you have listened to this paper.

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DISCUSSION.

MR. ACKER: I am inclined to think that this process in general is entirely feasible for the production of metallic sodium. There are several features in connection with the design of apparatus, here illustrated, which are interesting, but not altogether suitable for the purpose. I am not exactly clear, perhaps, concerning the object of one or two features of the apparatus, for instance, there is shown in Fig. 3, a magnetic coil, which is used for the purpose of agitating the electrolyte. What is the purpose of agitating this electrolyte, composed as it is of fused common salt? I should like to ask Mr. Ashcroft if I am correct in the understanding that it is desired to agitate the electrolyte by means of this magnetic coil?

MR. ASHCROFT: Yes. Also to circulate the lead sodium alloy.

MR. ACKER: If the process is conducted at a temperature which will produce the highest efficiency, it will be found that the bath, or rather the mass of salt in the furnace is not entirely fused and is anything but fluid. In decomposing molten common salt it is desirable that the temperature of the operation should be as low as possible, and for this reason small quantities of other salts are fed into the bath for the purpose of lowering the melting point of the mixture or increasing the fluidity thereof. It is so necessary to work at the lowest possible temperature that the bath is never, in practice, maintained in a perfectly fluid condition.

If the dry unfused salt is fed into the bath constantly or intermittently it does not at once fuse, but on the contrary, forms a pasty mass which does not quickly dissolve in the melt, and it is desirable and necessary to periodically break up this pasty mass by means of an iron bar or poker, unless indeed, the temperature of the bath is exceedingly high, and this should never be the case.

It would not be practicable to keep the bath entirely fluid unless indeed the salt was melted in a separate vessel and run into this apparatus in fused condition.

In operating with a fused electrolyte the space surrounding the anode or anodes is not large and roomy, as indicated in this drawing, but is necessarily confined, so that with more or less

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unfused and pasty salt surrounding the anode or anodes, and nearly filling this confined space, I think it will be apparent why the magnetic coil can hardly accomplish very much in the circulation of the electrolyte.

The liberation of gas at the anode, which, in a fused bath, takes place at a rather lively rate, owing to the exceedingly high current density employed, is instrumental to some extent in circulating, or at least agitating the electrolyte, and would probably do such work as well as or better than any other method. Possibly the author had in mind to prevent, by means of this circulation, the formation of the crust which under certain conditions forms on the surface of a lead cathode, in such an operation as this, after the current has been passing for some time? It has been my experience that the only way to prevent the formation of this crust is to increase the current density on both anode and cathode to a high degree and then the difficulty will disappear. The crust always forms with low current density, and is due to the settling of the heavy impurities in the salt, chiefly silica and iron oxide. The principle impurity, calcium sulphate, readily fuses with the salt, and does not settle to the bottom. It is surprising how much the presence of an additional one-fourth or one-half of one per cent. of silica and iron oxide will lessen the fluidity, or raise the melting point of the lower portion of the electrolyte. The so-called crust, on being removed from the surface of the lead, is generally a discolored mass of salt which looks as if it might be composed of 98 per cent. of iron oxide, silica and other impurities, and 2 per cent. of salt, but, as a matter of fact, it is simply common salt containing a higher proportion of impurities than the upper part of the melt. The total of these impurities may be only 2 or 3 per cent. in a crust which appears very hard and almost infusible in the bath. My use of the word "infusible," in this connection, of course, is relative, and refers to the melting of the crust while it is in the bath of fused common salt. If it is desired, for instance, to work the apparatus at 775 degrees C., as can be readily done without formation of a crust, by employing a suitable current density on the electrodes, it would be impossible to melt a crust in such a bath as this if it did form. The temperature might be raised 100 degrees or more, and even then the crust would not entirely disappear, but would simply become thinner and harder.

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By employing the correct high current density the impurities in the salt are to some extent eliminated. A portion, however, remains in suspension, and in the course of time causes a more or less pasty condition of the electrolyte in the bottom of the bath, but not a crust. It is then necessary to rake out this pasty mass by means of suitable tools. This operation is not difficult, but it must be done periodically, and for this reason the cover of the furnace must be removable, or built in sections, and so designed that the interior of the furnace will be entirely accessible. If a crust does form in the bottom of an electrolytic furnace, it is generally necessary to break it up by means of heavy bars, and sometimes sledge hammers. The formation of any crust should be absolutely prevented, however.

The secondary compartment of the furnace designed by Mr. Ashcroft would need to be much larger than the first compartment in order to permit working it at a comparatively low current density and low temperature.

The temperature in the first compartment might be about 775 degrees C. the current density 2,000 amperes per square foot and distance between electrodes three-eighths of an inch. The temperature of the alloy should afterward be lowered to 330 degrees C. or thereabouts, and then run into the second compartment, the contents of which should be maintained at 330 degrees C. The electrodes in this compartment—of which the molten alloy is one —should therefore be much larger than the other electrodes. The distance between electrodes could certainly not be less than three-eighths of an inch, and would probably be greater—so that, all in all, this compartment would probably be several times as large as the other.

The circulation of the lead sodium alloy between the two compartments does not present any difficulty whatever. It is easy to cause a definite and positive circulation of red hot molten lead sodium alloy, through channels from one compartment to another, and back again by simple mechanical appliances, and I should prefer such devices to the magnetic coil shown in the illustration.

In making these observations concerning Mr. Ashcroft's proposed apparatus for making sodium, I do not wish to detract from the value of his process. The employment of the lead sodium

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alloy in a secondary compartment, as an anode, and plating out the sodium therein, is excellent, and I am very glad to give due acknowledgment.

MR. CARL HERING: It seems to me that the form of motive power which Mr. Ashcroft uses for stirring his liquid will prove to be expensive in power; it is an extremely inefficient type of motor.

I agree with Mr. Acker that Mr. Ashcroft will probably meet with much trouble by the clogging up of those little holes. In his arrangement of cells the ampere-hour efficiencies of those two cells must of course be absolutely the same; if not, there will in time be either an accumulation of metallic sodium in the lead, or an attack of the lead because of an insufficient amount of sodium in it. I think Mr. Ashcroft will find that he will have to provide a shunt around one or the other of those two cells, so as to correct for this difference in ampere-hour efficiencies.

MR. ASHCROFT: That is done.

MR. C. F. CARRIER, JR.: I have been working for about two years on the same line as this process and encountered some of the difficulties mentioned by Mr. Ashcroft. It seems to me that there are several difficulties which he has not taken into consideration and which do not seem to be overcome in his apparatus. In the first place, there would be a great difficulty and a tremendous loss of heat in transferring that quantity of alloy from one furnace through a long regenerator to a second furnace.

In my work I used a composite furnace where the entire lead alloy was kept at the same temperature and that introduces a great difficulty. The cathode compartment is at a temperature nearly at the vaporizing point of sodium. At that temperature the caustic sodium is absolutely unfit for an electrolyte. I have experimented with different kinds of baths in the cathode compartment and find it possible to produce sodium in some quantity, but up to the present time the efficiency has been very poor. The difficulty with the crust on the surface of the lead is absolutely fatal to the apparatus as sketched here. Using the commercial grade of salt, within six hours the volt-meter will go up anywhere from 5 to 10 volts if you let that crust gather. Unless that crust can be removed the furnace has got to be stopped and cleaned out entirely; and it would seem that the heating in a pot-

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shaped furnace like that with no possible way of getting at the surface of the lead, would be rather impracticable. Has this furnace been in long continuous operation?

MR. ASHCROFT: The furnace which I used has worked for about three weeks continuously, but was not quite satisfactory in all respects. Some of the things you are speaking of now we find quite important; not all of them.

MR. CARRIER: Then the question of magnetic circulation: It struck me that there would be a difficulty there; you have a yielding medium. In a motor you have your lines of force in your armature passing through something that doesn't yield except to produce rotation. Here you have a yielding medium and your lines of force are going to be thrown out of position without causing mechanical movement and there is a loss of efficiency; so it seems to me it would take a good deal more energy to circulate that alloy by magnetism than it would by some mechanical means.

The use of a magnetic field to circulate a fluid metal cathode was patented July 3, 1900 by J. B. Entz, U. S. P., No. 652,761.

The conical collecting device in the cathode compartment was patented Dec. 11, 1900, by H. Becker, U. S. P., No. 663,719.

MR. ASHCROFT: The question of the patentability or otherwise of this process and apparatus is not what I was considering in this paper; but I believe Mr. Becker has not got a patent on that particular point of the collecting apparatus; and I acknowledge quite freely that the one illustrated is somewhat similar to his device. He has no patent on that at all.

I appreciate the great experience which Mr. Acker has had on these or similar lines of work and his endorsement of the main idea of the process I have described is very much to the point. His criticism of minor points I allow. The small holes outlined are not in fact what we used but are an addition due to a draughtman's imagination. If in practice they are found too small the simple remedy is to make them larger. In regard to the magnetic stirring the first point I would like to make is this: it is utterly indifferent whether a certain device for circulating small weights of material in such a process is efficient or is not efficient: it is something like trying to calculate what would be the most efficient thing to lift a spoon or a glass to the lips;

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you might have a means which was a hundred times less efficient and yet you would use it because it was the most convenient. The whole thing is apt to be trivial. It is a very convenient method of circulating the contents of a hot cell; and I can assure you, in my experience it works exceedingly well. Try a cell working at 3,000 amperes and I know of no means which can compete with the one I have described if you wish to agitate the contents. If agitation is not necessary in any particular work of course you will do without it, but if there is any reason why you do wish to agitate, there is no better means of agitating a hot cell than that. That is my experience. I have tried many mechanical devices.

The question of small holes: as a matter of fact the small holes have never been used and I don't know that they ever will; but they have been drawn like that by draughtsmen and they might stop up, or they might not. The next question about the difference in the sizes of the two cells, what Mr. Acker said is perfectly true. I think the proportion between the cells is shown better on Fig. 1; and I think is is about 4 to 1.

Really the only novel part of this process is in the caustic end; and the only patent in the process of any value beyond certain details of apparatus is in using an electrolyte that is not consumed with a soluble anode. I regret that I cannot give you all the details of the work which the staff of the United Alkali Company have done on this process; for obvious reasons certain matters of that sort are not to be published but I have told you all I rightly can.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

LABORATORY RESISTANCE FURNACES.

By G. R. White.

It has been found possible to make both carbide and carborundum in the laboratory with small resistance furnaces. The furnace is built up of ordinary bricks, and the length of the resistor is about 6 inches. An alternating current of 110 volts and 200 amperes was used, but the best results were obtained by using from 150 to 175 amperes.

The most satisfactory results were obtained by connecting the leads to two graphite bars by means of copper plates which were drawn together by bolts. One copper plate was placed on the under side of the block, a second on the upper side, the lead wire was placed between the second and a third plate, and the three plates were then drawn together by bolts. This insured very good contact. Into each of the graphite bars a hole was bored, and into these holes a carbon rod, whose diameter was 6 mm and whose resistance 0.5 ohms, is tightly fitted. These rods were obtained from the National Carbon Company, of Cleveland, Ohio. The line current was cut down by a water rheostat.

One of the difficulties experienced was that the rods sooner or later burned out, and when this occurred, the high resistance of the charge cut off the current completely. This difficulty was overcome by packing a layer of finely powdered graphite or carbon around the rod for the purpose of protecting the rod from the oxygen of the air. With this precaution, it was found that the rod would remain intact for over an hour, and that the yield of carborundum was very satisfactory with a run of this duration.

The charge consisted of 55 parts of a good grade of sea sand, 35 parts of ground coke, 2 parts of salt and enough sawdust to make the mass porous. This charge was tightly packed around the rod, and a current of about 150-175 amperes was passed.

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The voltage between the terminals was from 30-35, and this increased by degrees as the run progressed, owing to the increased resistance as the rod gradually burned out. The charge grows hotter and hotter until, with a slight explosion, the carbon monoxide forces its way to the outside, and there burns with a blue flame. On cooling, it is found that the product is arranged in concentric rings, just as found on a large scale. The arrangement in rings is as follows: First, the layer of graphite; second, the crystallized carborundum, which gradually shades away into "siloxicon," and finally, volatilized silica, which is scattered through the cooler portions of the charge, and especially on the bricks used to cover the furnace.

It was also found possible to make carborundum by constructing a core of crushed carbon, which was obtained from the National Carbon Company. The core is first packed, and then fine graphite powder is sifted over this, in order to prevent arcing between the particles, and to insure good contact all the way across. This method has the disadvantage of requiring a longer time than the other, and the heat is not so intense as with the rod. An intensely localized heat seems to be necessary for a good yield of carborundum. The core of crushed carbon, in order to conduct well, has to be about 1¼ inches in diameter, and it requires some time to bring a core of this size to the necessary temperature.

Furthermore, it is also possible to make calcium carbide by this method. The procedure is just exactly the same as in the case of the carborundum. By use of a current of 150-175 amperes, a very good carbide was obtained near the rod.

In conclusion, the idea of using a small carbon rod as a resistor is due to Borchers. The preparation of carborundum and carbide, as described, furnishes a very instructive laboratory experiment. The materials used in constructing the furnace are cheap, and only a fairly large current is needed. Furthermore, the factory conditions are very closely paralleled, especially in case of the carborundum. By continuing the run for four or five hours a very compact carborundum can be obtained, and furthermore, crystals measuring 1 mm. on a side are often found.

Cornell University.

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DISCUSSION.

PRESIDENT BANCROFT: In this particular form the furnace is very satisfactory for laboratory practice, especially when you have not very much power available; and it is for that purpose (regular work of instruction) that we have been using it. As I mentioned yesterday, when the run takes place successfully we get a very nice result with a white circular line of silica on the extreme outside of the zone in which the action is taking place.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

ELECTROCHEMICAL PROCESSES AS STATION LOAD EQUALIZERS.

By E. A. Sperry.

For some years the station manager, the electro-chemist, and the electro-metallurgist have been groping for each other. I say groping, because for some reason there is a notable lack of any union of interests or any electrochemical process deriving its supply or utilizing equipment of the central station. Papers have been read and much said as to the possibilities of this combination, which, however, does not seem to materialize.

Some time ago I undertook some investigations as to the exact conditions existing with some central stations, and what terms they were willing to make as inducement to the establishment of permanent electrochemical loads of more or less magnitude. One prime requisite with electrochemical processes is cheap and centrally located power; and many of these processes may easily become large consumers of power.

The question naturally arises, why is it that this combination has not been brought about, as earlier expected. The result of my observations and of such time as I have been able to devote to the question, has been that neither party has, as yet, by any means exhausted this subject, and, furthermore, that some misunderstanding exists as to the conditions which are capable of being so harmonized as to yield commercial results to both.

The condition is growing more favorable in that the Central Station manager is constantly gaining knowledge and experience as to the value and relation of certain factors in his load curve, and something as to what it means to him to have the valleys filled, portions of his load equalized, and the mean load increased. We hear much about the evils of the peak in the station load curve; the peak in the load curve is only a relative matter, and there are managers who still think that the disadvantages of peak

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load is a matter of altitude of the peak. Not at all so; on the contrary, it is only a matter of prominence above surroundings, and its evil is in its height in relation to mean load. *The peak represents the investment,* while *mean load represents receipts.* Anything that brings up the latter, contributes directly to earning capacity, and (a point which is not generally recognized in this connection) almost wholly independent of the rate received for the additions if they are rightly placed on the load curve.

Another favorable sign is that managers are becoming more and more keen for business, and as their stations increase in importance, are able to make concessions and inducements for loads impossible a few years ago, and, in many instances, are willing to make very low rates for strictly "off peak" load. The operation of the stations vary through quite wide limits as to the hours and seasons at which they can furnish current falling strictly within this class. With the very closest prices that have been named, the station manager has, in some instances, demanded the emergency privilege of cutting off the current always with notice, unless absolutely impossible, and, in one or two instances, the price has been made on a sliding scale, based on the price of fuel. In connection with this last item, any long-time contract should include considerations relative to the conversion factors or the thermal efficiency of the prime movers employed in such a way as to properly cover the actual fuel factor, as represented in the power cost, in the mutual interest of parties concerned.

The hours and seasons available in various stations, I find to fall within three classes. The most favorable being a guarantee of twenty-four hour power for ten months of the year, approximately, or forty-three weeks; three weeks, twenty-two hour power, and six weeks, twenty-hour power, during these two latter periods guaranteeing forty hours continuous power at the weeks' ends. This gives full year, less 180 hours, or about 98 per cent. available time throughout the year. *The second class* grants twenty-four hours during about nine months of the year, or thirty-nine weeks; six weeks with twenty-one hour power and seven weeks with nineteen hour power, guaranteeing during these two lafter periods, thirty-eight hour continuous power at the weeks' ends. This class yields 96½ per cent. of all available time. *A third class* demands a two-hour peak for six days each week, during which no power

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is furnished for ten months, or forty-three weeks, of the year, and a four-hour peak during the remaining nine weeks. This class is willing to guarantee throughout the year, forty-hour continuous power at the weeks' ends, which yields 92.6 per cent. of the total time available.

Some station managers, especially those of the first-class, go so far as to say that if they assume the load, they will, in all probability, carry it more hours than guaranteed. Others, again, go so far as to intimate that they will find some way in which to carry it all the time, especially days when their battery is not unduly drawn upon. In every instance, the cost will go higher if the energy is required to be transmitted to a distance, and the site for the electrolytic plant should be chosen accordingly.

It may be stated as a general proposition under these conditions, where the electrolytic load is available to equalize the station load, that power is available for electrolytic work in large units at equal rates, if not more favorable than those ruling for water power. Where the process is one that does not admit of interruption, storage is, of course, always available, where the extra cost entailed permits its use. There are conditions under which the additional power cost entailed need not be great, and from the standpoint of the Central Station manager, a storage battery is a most desirable adjunct. This arises from the fact that while its discharge is confined to short and definitely placid periods, its charge may go forward at periods entirely conformable to the demands of the station for equalizing purposes, while its economical rate of charge may be varied through exceedingly wide limits, therefore available for the most economical loading of the generating units.

In some electrolytic processes, the current may be dropped to a mere fraction of normal intensity, and, in this way, a comparatively small storage battery may be employed to carry the process over the cut-off periods.

Intermittent processes or those susceptible of interruption under commercial conditions, are desirable in this connection. The electrolytic and electrothermic arts by no means abound in processes that may be considered commercially intermittent. It is expected that this condition will change gradually as the advantages of centrally located, abundant, and cheap power, are

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brought more into prominence; this is evidently the duty of the station management having problems of load and equalization before them. On the other hand, the electrochemists and metallurgists should be none the less active. In fact, it would seem that their task is the greater. Processes that are applicable must be brought out, thoroughly tested, under conditions of service proposed, and demonstrated to be thoroughly practicable and commercial.

From the promising commercial results certain to follow the successful prosecution of this work, it is evidently worthy of patient and intelligent effort on the part of the best talent at the command of each of the parties affected.

DISCUSSION.

PRESIDENT BANCROFT: This is a paper on which the professional man is better qualified to speak than the university man. It seems to me to be a question of where can you find suitable intermittent electrochemical processes.

MR. C. F. CARRIER, JR.: I talked with the manager of the power station in Elmira in regard to this subject. The lowest for which he seemed to think that it was possible to furnish current was just a little under 1c per kilowatt hour. That price was so much higher than current can be obtained from water power that I did not think there was much hope for it in Elmira. They will furnish current for only 18 hours a day.

MR. E. A. ASHCROFT: I agree, to a certain extent, with what Mr. Carrier said. I have had that problem before me a good deal, using intermittent load equalizers. I think it would be very interesting if Mr. Sperry would tell us what prices such power can be furnished at. As to the question can intermittent furnaces be found to use them cheaply? I have no doubt at all that such processes can be found if the power can be produced cheaply enough, but it is after all solely a question of dollars and many water powers produce power at so low a rate that it seems probable that no station manager would consider it worth while to collect such prices.

DR. J. W. RICHARDS: Mr. Sperry speaks of the electric pro-

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cesses; but almost all electric processes are continuous; and it is practically electro-thermal processes which are the intermittent and desirable ones. If, for instance, the plant could furnish 19-hour power, a process of making carborundum with 19-hour runs could utilize such power very well and efficiently. I think it is the electro-thermal processes which are mostly the intermittent ones and which will be most likely to utilize these fractions of a day by adjusting the length of their operations to the length of time during which they can get the power.

MR. SPERRY: Prices have been made which vary between 28-100ths and 41-100ths of a cent per k. w. h., this is on a basis of $18.00 to $26.50 per h. p. year; 31-100ths of a cent per k. w. hour, is on a basis of $20.00 power. In many instances this can be obtained D. C., which is somewhat more favorable than that furnished A. C., as for instance at Niagara Falls, where the operating company is compelled to suffer the conversion losses. The whole point is, that almost any sum that can be realized by the station manager for power which is not used during the peak-load, and which can be employed for equalizing purposes, is "velvet," as the expression goes, and some of the managers are coming to realize this fact.

A banked fire is fuel at the lowest possible efficiency; some forms of equipment are better running than idle and the pay roll is not affected and the economies of steadily loaded units, are considerations that all have their effect. The station manager has a large and expensive equipment, which should be utilized as the generating plant for the electro-chemist and electric furnace worker.

I think as Dr. Richards has suggested, the electro-thermal engineeer, as well as electro-chemists, should make an earnest endeavor to utilize the equipment of a central station manager if possible. I think a good lively interest will be found on the part of some central station managers and they will meet us cordially and with a commercial proposition, if on our part we can find something that is intermittent and applicable.

MR. HENRY HOWARD: These large power stations produce, of course, an immense amount of exhaust steam which is disposed of in condensers, but which they might be willing to sell for evaporating purposes for use with vacuum pans, triple effect

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evaporators, etc. I looked into this matter two or three years ago in connection with the Edison Electric Company of Boston. The proposition was to use their exhaust steam in a triple effect evaporator for evaporating sea water for the production of salt. This proposition is, of course, only applicable to those stations on the sea-coast; the only reason that the project was abandoned was for the want of a triple effect evaporator which could successfully handle the incrustations which form during the evaporation of sea water. If such a machine could be perfected the proposition would undoubtedly be quite a profitable one for those plants which are located in coast cities having to pay a considerable railroad freight from the salt mines. The exhaust steam could also be used in certain electrolytic processes where a good deal of evaporation has to be carried on. One point that should be remembered is that a much cheaper engine plant can be profitably installed when the exhaust steam is to be sold at atmospheric pressure.

PRESIDENT BANCROFT: In connection with that, the Remington salt plant, which we are going to visit tomorrow, provides the electricity for the lighting and street railway in the city, and uses the exhaust steam for evaporating their salt brine; so that here in this particular town those two things are being run together.

MR HOWARD: Do they use single or triple effect?

MR. CARRIER: I have been told they use an ordinary vacuum pan, using some live steam mixed with their exhaust steam, The salt crystallizes on the pipes with exhaust steam alone and soon clogs up the vacuum pan; so they have to use a little live steam to make the salt boil violently enough to loosen the crystals from the pipes.

MR. SPERRY: In Cleveland they conduct the exhaust steam from the entire railway plant some two blocks in a 48-inch cast iron main to the Cleveland Salt Company and there evaporate brine to salt, as has been suggested here; and there they do it in a single vacuum pan, no live steam is used and little or no salt incrustation is encountered. Incrustations from calcium sulphate however are troublesome. That which is not removable by live steam is dislodged by air drills.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

THE ELECTRIC VACUUM FURNACE.

BY WM. C. ARSEM.

I. HISTORICAL.

Previous work in vacuo at high temperature has been confined to experiments with quartz and porcelain tubes.

Schuller distilled and sublimed various elements and compounds in evacuated quartz vessels. The boiling points of many metals have been determined in evacuated porcelain tubes by Kahlbaum, Roth, Siedler, Krafft, Bergfeld, Lehmann, and others. In all cases, however, the vessels were subjected to external atmospheric pressure, and the scope of the experiments was limited by the temperature at which they collapsed. Porcelain collapsed between 1,400° and 1,500°, and quartz at somewhat higher temperatures. Moreover, certain metals and other substances which attack quartz and porcelain could not be investigated.

In the electric vacuum furnace described below, the attainable temperature is limited only by the vaporization of carbon, and crucibles of any material suitable for a particular experiment may be used.

II. DESCRIPTION.

The vacuum furnace is a special type of resistance furnace, enclosed in a vacuum chamber, with means for continuous cooling of the parts liable to be injured by excessive heating, and so designed that the effect of heat on any substance or the course of any reaction may be studied up to the vaporizing point of carbon, the substance in the crucible always being visible through a window.

A calibration of the furnace to determine the relation of the temperature to the energy, makes possible the accurate control of the temperature. The advantages of a vacuum for protecting the heater and the substance being heated, are obvious.

It consists of an air-tight metal vessel, with tubular electrodes

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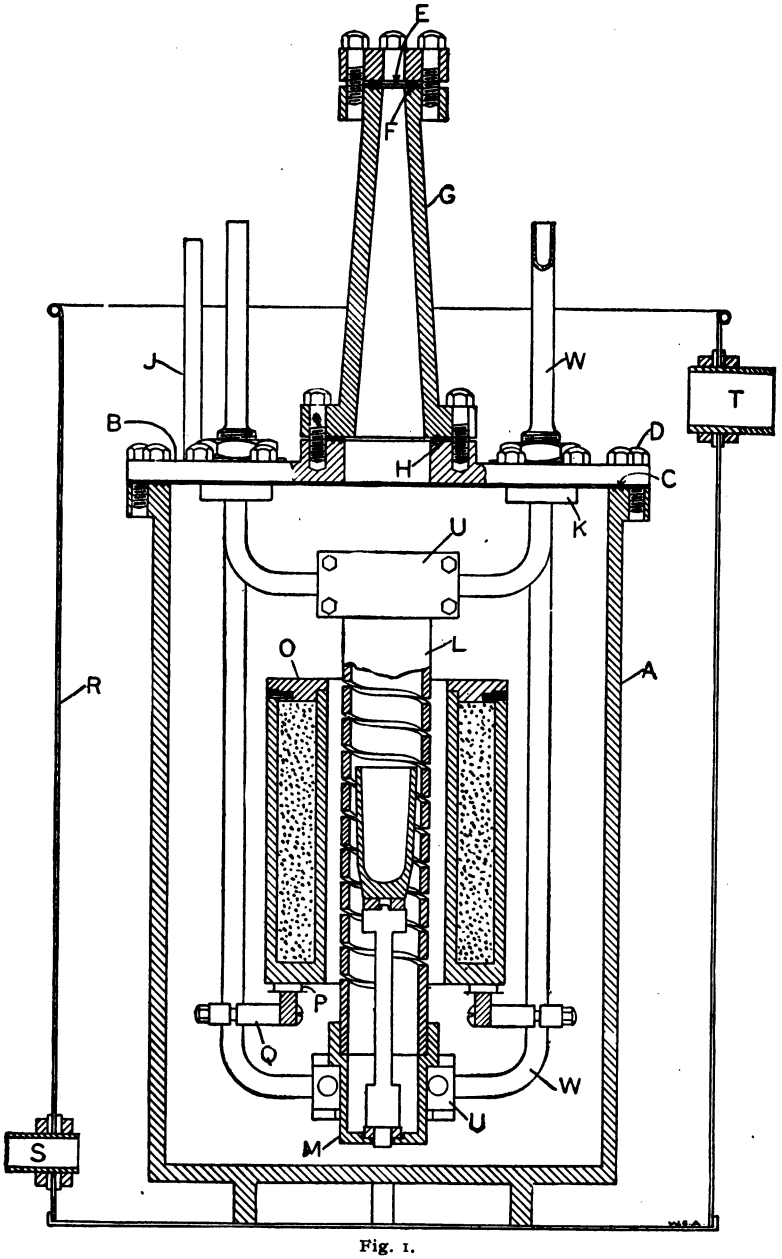

Fig. 1.

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entering the cover. These electrodes are provided with clamps which hold the heater in place and make contact between it and the electrodes. The radiation screen which surrounds the heater to diminish the radiation loss is also held in place by supports attached to the electrodes. The metal vessel stands in a can which serves as a water jacket. When the furnace is running, a constant flow of water is maintained through the water jacket and through the tubular electrodes.

The construction will be better understood from Fig. 1, which is a sectional elevation through the center. The chamber, *(A)*, and cover, *(B)*, are castings of gun-metal turned true at the joint. A lead gasket, *(C)*, 1-16-inch thick, forms an air-tight joint when the cover is fastened down with the cap-screws, *(D)*. The first time the furnace is assembled, the tightening of the screws forces the lead into the annular grooves of the chamber and cover. The ridges thus formed in the lead washer, and suitable reference marks on the cover and chamber, make it possible to replace the parts in the same position after opening the furnace for cleaning or repairs. Leakage due to porosity of the castings is prevented by applying a thin coat of solder all over the inner and outer surfaces of the chamber and cover, after turning to dimensions. The chamber has four legs to permit the flow of water underneath. The tube *(J)*, through which the air is exhausted, is soldered into the cover.

The window, *(E)*, is a disc of clear white mica about 0.005-inch thick, clamped between two lead washers, *(F)*, by means of a brass cap and four cap-screws. The brass surfaces touching the lead washers have annular grooves into which the lead is forced by the pressure. The window tube *(G)*, is of gunmetal, and is fastened to the cover by six cap-screws, the joint being made tight by a lead washer, *(H)*.

The electrodes *(W)*, are formed of brass tubing, bent into shape. The threaded brass bushings *(KK)*, which constitute parts of the electrode joints, are soldered to the electrode tubes.

The construction of an electrode joint is shown in detail in Fig. 2. Two lead washers *(W_1W_2)*, separated by a mica washer, are interposed between the cover and the flange of the bushing. The bushing is insulated from the cover and the upper lead washer, *(W_2)*, by the fibre sleeve *(S)*, and the nut *(N)*, is

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insulated from the cover by the fibre washer *(F)*. The fibre parts are impregnated with paraffin to make them waterproof. By tightening the nut *(N)*, a perfectly tight, electrically-insulated joint is obtained.

The heater clamps, *(UU)*, Fig. 1, are of copper.

The heater, *(L)*, is a helix of conducting material such as carbon or graphite. Artificial graphite is preferred for high temperature work, because of its freedom from impurities. Metallic heaters can be used for some purposes and have certain advantages, one of which is the inability to absorb air when cold. A heater is made by sawing a slot in a hollow graphite cylinder. Its dimensions and the number of turns are so related that at the

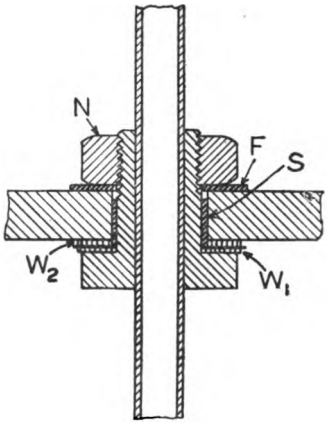

Fig. 2.

highest temperature reached, the potential difference across the heater shall not be much more than 50 volts, in order to avoid excessive Edison effect and the tendency to arc across to the screen Good results have been obtained with a heater 2 inches outside diameter, 1⅝ inches inside diameter, and having ten turns in a length of 7½ inches. The graphite cup, *(M)*, holds the lava insulating ring on which the crucible support rests. The proximity of this ring to the cold bottom of the furnace prevents it from fusing or being made conducting by heat.

The radiation screen, *(O)*, is a double-walled cylindrical box of Acheson graphite, filled with graphite powder. Its purpose

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is to minimize loss of heat by radiation. Owing to the low thermal conductivity of the powdered graphite, the inner wall of the screen becomes nearly as hot as the heater, and then the rate of radiation from the heater to the screen, which depends upon the temperature difference, becomes very small, and equal to the rate at which heat is conducted away through the graphite

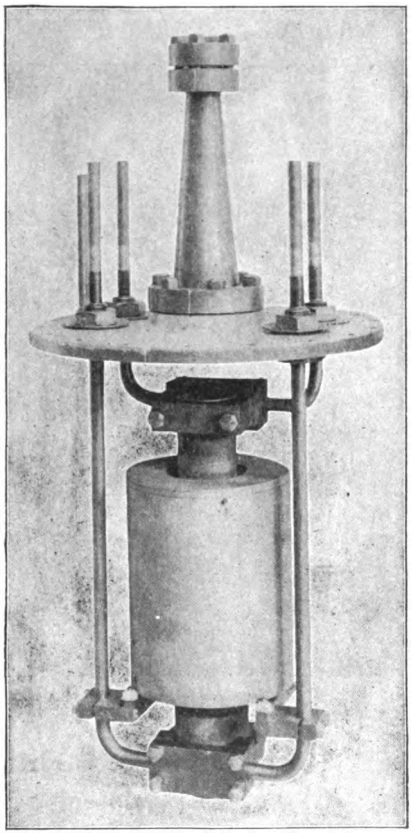

Fig. 3.

powder. It was found that with the use of the screen, the melting point of platinum could be reached with but one-fourth of the energy necessary without it. The screen is supported by the copper arms, (Q), from which it is insulated by the lava buttons, (P).

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The water jacket, *(R)*, is a galvanized iron tank provided with an inlet, *(S)*, and an outlet, *(T)*.

Fig. 3 shows the interior parts of the furnace raised out of the chamber. In Fig. 4 are shown two vacuum furnaces which have had almost constant use for two years. These have no window tubes, but the windows are fastened directly to the cover of the furnaces.

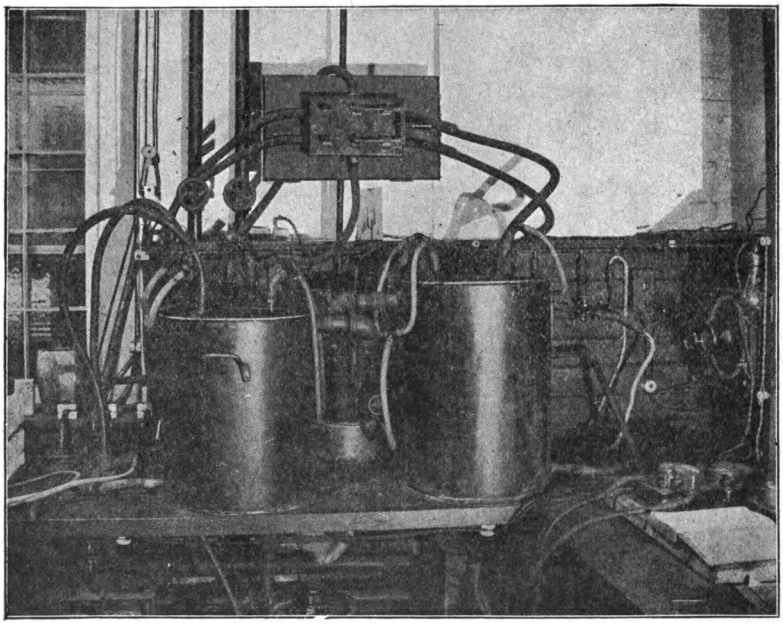

Fig. 4.

III. Crucibles and Crucible Supports.

The choice of material for crucibles is determined by the nature of the substance to be heated and the temperature reached. Graphite crucibles are used when the substance to be heated is not acted upon by carbon, and are conveniently made from solid rods of Acheson graphite.

Magnesia crucibles are frequently used for fusing metals and preparing alloys when the temperature to be reached does not exceed 1650°. These crucibles are made by strongly compressing

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in a steel mold, by means of a hydraulic press, a mixture of finely powdered and sifted magnesia, with a suitable binder. A porcelain kiln was used for firing the magnesia before using and for baking the crucibles, the temperature attained being about 1350° C. Crucibles made from magnesia fired at a lower temperature, are very liable to crack, owing to the great shrinkage which they undergo between 1200° and 1600°.

Other metallic oxides have been found to be more suitable than magnesium oxide as crucible material. In many cases, oxide crucibles must be separated from the graphite support by a refractory metal cap, to prevent reduction at the contact surface.

Crucibles of iron, copper, fire-clay, porcelain, and thorium oxide, have been used for special purposes, the latter substance withstanding a higher temperature than anything else tried, except graphite.

In Fig. 1, a crucible and graphite support, with a metal cap, are shown partly in section.

IV. Accessory Apparatus.

Vacuum Pump—A double-cylinder Geryk oil-pump is used with the cylinders in series. It gives a good vacuum in the furnace fifteen minutes after starting. The pump is connected to a brass main-tube having soldered branches, to which the furnace, gauge, and air inlet valve are connected by means of heavy rubber pressure-tubing. The joints are made tight by brass sleeves, the ends of which are filled with a wax mixture. Brass stopcocks were first used, but were later replaced by mercury-seal glass cocks, which did not leak.

Vacuum Gauge—A closed mercury gauge of the manometer type was used at first, but it gradually became soiled, and an uncertain capillary error was introduced, which made it unreliable for accurate measurements. To avoid this, the gauge is now connected through a tube containing glass wool and potassium bicarbonate crystals, to retain dust and acid vapors, with an auxiliary tube containing a drying agent.

Electrical apparatus—The current is furnished by a single-phase alternator in connection with a step-down transformer. Regulation of the current is effected by means of rheostats in

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the generator field circuit. The measuring instruments are of the Thomson inclined-coil type. The voltage is measured directly, the current being first reduced by a current transformer.

V. Operating Conditions.

Vacuum—When all joints have been properly tightened, the pressure can be reduced to a fraction of a millimeter of mercury. If leaks are suspected, the furnace is closed, the jacket is filled with water, and compressed air is forced into the chamber. Leaks are shown by air bubbles. If due to defects in the casting, they can be repaired by soldering, or, if not too large, by painting with pyroxylin lacquer. Leaks at the electrode-joints may occur when a new furnace is first assembled, but these disappear when the nuts are tightened sufficiently. The vacuum becomes somewhat poorer as the temperature in the furnace rises, especially with a new heater and screen, owing to the escape of gases from the graphite or from the substance which is being heated; but on maintaining the temperature at a definite point, the vacuum finally improves up to the starting value.

A high vacuum can be maintained even at the vaporizing point of graphite.

Description of Run—The crucible is placed on the support and centered so that it does not touch the heater, the window tube is then fastened down, the washer and contact surfaces having been first carefully cleaned. When a good vacuum has been established, the current is switched on and the water allowed to flow at such a rate through the jacket that it comes out barely warm, the water-level being above the window joint. Water is also passed through the electrode tubes, the outflow being allowed to play against the side of the window tube. In most cases, the current should be raised gradually, so that the behavior of the heated substance can be followed.

The substance or article being heated is observed through a mica window, colored glass being used to protect the eyes at temperatures above 1100° C. At 2500° C. and above, three or more thicknesses of blue glass are necessary to make it possible to distinguish the outlines of the substance, because of the intensity of the light.

When the desired result has been obtained, the circuit is opened.

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From one to three hours are allowed for cooling, according to the temperature reached, then the water is let out of the jacket, air is admitted to the furnace, the window-tube is unfastened, and the crucible is removed.

VI. Temperature Estimation.

Owing to the small total heat capacity of the heater and screen, the temperature very soon reached a constant value for each value of the energy used, and it is therefore possible to calibrate the furnace so that the relation of temperature to energy is known.

For this purpose, the melting points of copper and platinum were taken as fixed points, and the amounts of energy required to maintain these temperatures continuously were determined the procedure being as follows

Some pieces of electrolytic copper were fused in a graphite crucible, so as to obtain oxygen-free copper with the melting point, 1084° (Holborn and Day). The current and voltage were read just when fusion began. The current was then diminished until the copper solidified, and was then gradually raised about one ampere every five minutes until the copper melted again. This procedure was repeated a number of times, and the product of the lowest average values of the current and voltage was taken as the energy corresponding to the melting point of the copper. Fusion of the globule was characterized by the appearance of a dark spot on top, this being the only part of the globule which reflected no light vertically upward. Freezing of the globule was accompanied by the disappearance of the dark spot when the copper crystallized and the surface was no longer smooth.

A piece of c. p. platinum wire was heated in a small cup of thorium oxide inside of a graphite crucible. The current was very gradually raised as the melting point was approached, this having been approximately determined previously. The readings were taken while beads of melted platinum were slowly forming on the wire. The melting point of platinum was taken as 1780° C. (Le Chatelier.)

To find a mathematical relation between the energy and temperature, the observed values were tried in various well-known formulæ, and it became evident that only an exponential equation would answer.

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The expression chosen was $y^n = ax$, in which y represents the temperature of the crucible above that of the room, x is the energy in kilovolt-amperes, and n and a are constants. For convenience, the equation was used in the form $(y - 20)^n = ax$, or $n \log(y - 20) = \log a + \log x$, in which y is the actual

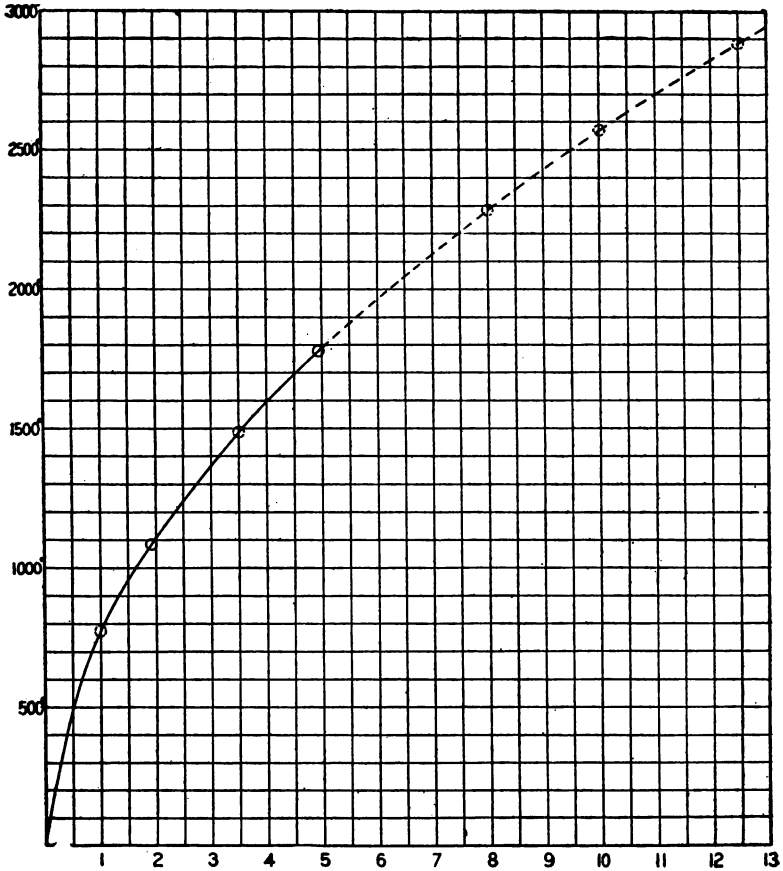

Fig. 5.

temperature (centigrade) of a crucible at the middle of a heater the average temperature of the water in the jacket at the start, 20°, being taken as the temperature of the surroundings.

The average values found by the experiments described, were:

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Temperature	Kilo-volt-amperes
(20°)	(0.0)
1084°	1.909
1780°	4.953

From these values, the constants were calculated as follows:

$$n = 1.895$$
$$\log a = 5.4552$$
$$a = 285200$$

The curve (Fig. 5) was plotted from the results obtained, the dotted portion being continued through extrapolated points calculated from the equation.

Accuracy of Calibration—The principal source of error was the slight variation of the generator voltage. The variation at the melting point of platinum was 4.915 to 4.992 K. V. A., corresponding to an uncertainty of 25° in temperature.

If the equation holds at higher temperatures, the error thus introduced into the constants will make measurements in the neighborhood of 3,000° uncertain by 50°.

I hope later to check these calculations by an optical pyrometer, which should give accurate results, since any substance heated in the furnace, being enclosed by walls at the same temperature, will radiate like a black body.

The calibration up to 2,000° is at least sufficiently accurate for practical purposes. In one experiment, the furnace was running constantly day and night for ninety hours, keeping the temperature very close to 1,800°.

(No correction was made for the small current which flows through the water between the electrodes.)

VII. Edison Effect.[1]

In one of the first forms of the furnace, the radiation screen was supported by the lower clamp, and the crucible support was also in electrical contact with the clamp, as shown in Fig. 6, the need for further insulation being then unknown. With such an

[1] T. A. Edison, 1884.
Preece, Proc. Roy. Soc., 38,219; (1885.)
Fleming, Proc. Roy Soc., 47,118; (1889.)

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arrangement, a rise of current and a simultaneous fall of voltage was observed as the temperature approached 2,000 C., and an arc would soon start at the point A, Fig. 6. This was found, by the arrangement shown in Fig. 8, to be due to a discharge taking place across the space between the heater and the screen. The heater being at a slightly higher temperature than the inside of the screen, an excess of current flowed across the space in such a direction that the heater was negative, and amounted to two amperes at times. The arrangement was first calibrated by passing a direct current through the shunt and meter in

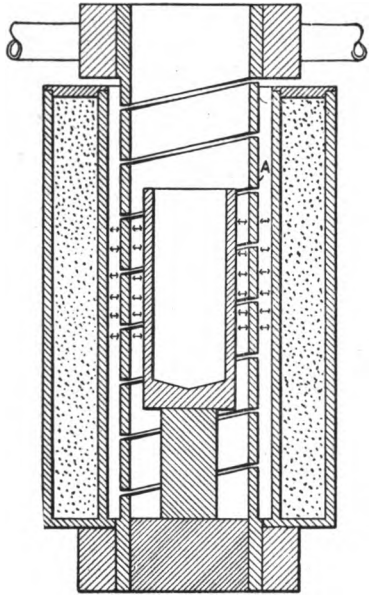

Fig. 6.

parallel, and noting the reading of the meter for each value of the current.

In a later form of the furnace, with the screen and crucible support both completely insulated from the heater (Fig. 7 and 8), a similar variation was observed, but of much smaller magnitude, and there was now no tendency to arc across. The relative variation in the two cases is shown in Fig. 9. The paths of the discharge in the two cases is shown by the arrows in

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Figures 6 and 7, and by the black coatings found on the heater, screen, and crucible after a high temperature run.

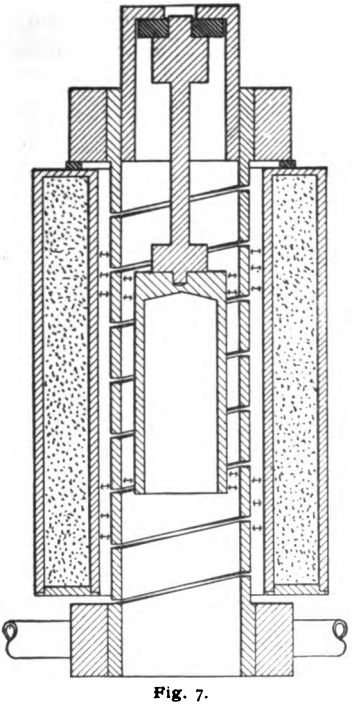

Fig. 7.

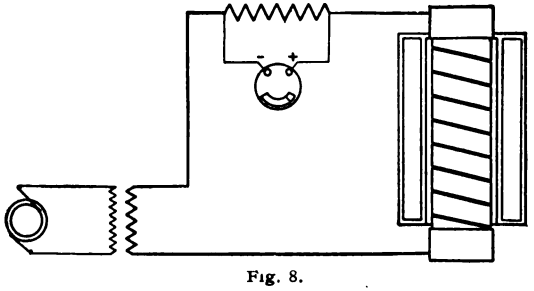

Fig. 8.

The ease with which ionization takes place at high temperatures is thus shown in a striking manner.

In Fig. 10, *b* and *c* show the deposit produced on the heater

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and crucible at high temperatures, with the arrangement shown in Fig. 6. The location of the arc is shown in *a*, Fig. 10, the black deposit being brushed off to show clearly the disintegration which has taken place. Fig. 11 shows two crucibles with the double ring deposit obtained with the furnace arranged as in Fig. 1 or Fig. 7.

To pass a discharge through a rarefied gas, as in a "vacuum tube," requires a certain fall of potential, mainly at the cathode. During the passage of the discharge, the cathode is disintegrated, the detached particles moving normally from the surface of the cathode, and depositing on the nearest surface.

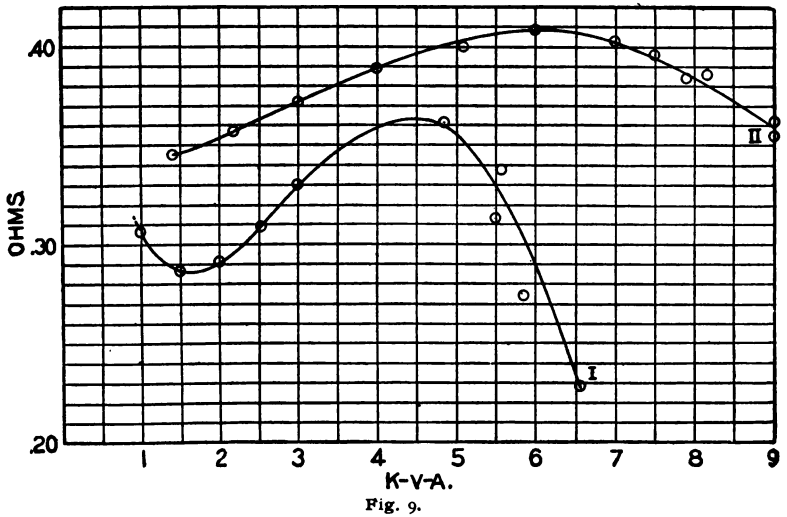

Fig. 9.

It is well known that the cathode-fall diminishes as the temperature of the cathode is raised.[2] When the cathode becomes hot enough to have an appreciable vapor-pressure, the glow discharge becomes an arc.[3]

We therefore have in the furnace, a complete analogy to the phenomena in a vacuum tube. The points between which the small arrows are placed become alternately anode and cathode to the alternating current which leaks between them through the ionized gas, so that the erosion takes place on both surfaces.

[2] Cunningham, Phil. Mag., *9*, 193.
[3] Hittorf. Ann. d. Phys. *21*, 90; (1884.)

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The gradual, apparent lowering of the resistance of the heater with rise of temperature, shown by the curves in Fig. 9, is due to the increasing leakage of current across the space where the arrows are. With the furnace arranged as in Fig. 7, there are two discharges in series. Between the two rings there was not a great enough potential difference to maintain two discharges.

Two explanations are possible for the presence of the rings:

1. A certain minimum potential difference is required to produce a discharge at a given temperature, just as there is for an arc. This minimum is then just half that across the

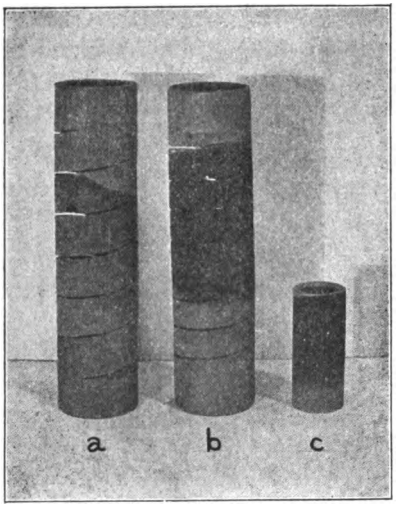

Fig. 10

unblackened space on the heater between the rings, and lies between ten and fifteen volts.

2. The resistance along the path taken by the discharge may be less than the resistance of the heater between the rings.

The second explanation seems inadequate, as it does not account for the complete absence of deposit between the rings. I consider the first explanation more satisfactory.

In the type of furnace shown in Fig. 1, the Edison effect is much reduced by using a heater of lower resistance, so that a lower voltage is required to reach a given temperature, and by making the space between the heater and screen wider. Both

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the screen and the crucible support are insulated from the heater. The black rings of deposit are now produced only at the highest temperatures (2,500° and 3,000°).

VIII. Applications and Results.

The furnace is especially useful for the fusion or heating of substances at temperatures beyond the range of the ordinary gas furnace, but which cannot be conveniently handled in the arc furnace because of the excessively high and unmanageable temperature and the presence of carbon vapor. The temperature can be kept constant within less than 25° for any length of time.

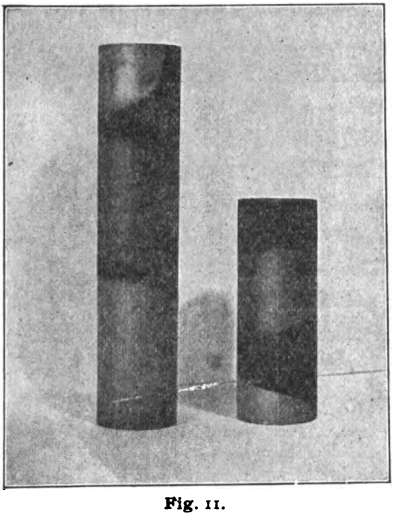

Fig. 11.

It makes many experiments possible at high temperatures in the absence of chemically active gases.

Above 2,200°, work is somewhat restricted by the lack of a crucible material which does not fuse or vaporize, or is not attacked by carbon or the substance to be heated.

Metals obtainable only in the form of a powder containing impurities can be brought into a pure compact state by fusion in vacuo, as the non-volatile impurities form a separate layer, and the volatile ones can pass off. Other substances which cannot be heated in air without oxidizing, can be fused in vacuo

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without difficulty, unless they vaporize below their melting points. Aluminum oxide, platinum, and other refractory metals have been fused. Magnesium oxide, iron, silicon, and aluminum have been vaporized.

Alloys of exact composition can easily be prepared by fusing

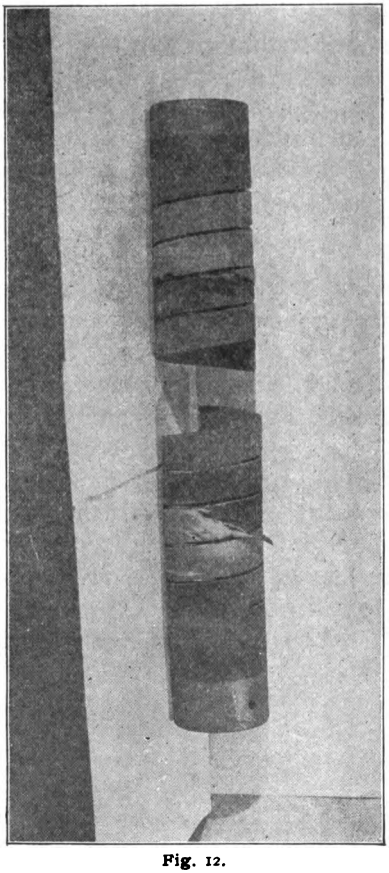

Fig. 12.

their components together. In this way, a number of iron alloys have been made.

Chemical reactions, syntheses, and reductions can be carried on with great facility under direct observation. Gas-producing reactions can be followed closely by means of the manometer,

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which shows the temperatures at which the reaction begins, and the point at which the reaction is over.

The calibration of an optical pyrometer could be easily performed by comparing it with an electrical resistance pyrometer or a thermo-couple heated in the furnace; since any substance heated in the furnace, being enclosed by walls at the same temperature, will give "black-body" radiation.

Melting points of metals, compounds, firebrick, and other refractory substances can be determined within a few degrees by reference to the calibration curve of the furnace, and still greater accuracy could be obained with an optical pyrometer.

Substances could be distilled for purification or separation. Magnesium, zinc, and cadmium have been thus distilled.

IX. Vaporization of Graphite, and Life of Heaters.

At high temperatures, the middle of the graphite heater slowly vaporizes, and the sublimed graphite condenses on the colder parts of the heater and radiation screen. Finally, the heat tends to become more localized at some thin spot, which rapidly wastes away until a break occurs and an arc starts. This point is indicated by a sudden *drop* in voltage, because the arc so extends itself that one or more turns are short-circuited.

Fig. 12 shows a broken heater with the partly loosened skin of sublimed graphite. This sublimed graphite has an almost silvery whiteness, and under a low power microscope shows a botryoidal surface.

The average life of a heater at different temperatures is shown by the following table:

Temp.	Life
2500	9 hours
2700	3¼ "
2900	2 "
3000	1 "
3100	¾ "

These results are for hand sawed heaters. Machine cut heaters being more uniform, will probably have a somewhat longer life.

Since carbon vaporizes from the anode of a carbon arc at about 3,700° C., at atmospheric pressure, it is to be expected

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that in vacuo it would vaporize at a much lower temperature. It is therefore very probable that the temperature measurements calculated from the extrapolated part of the curve are fairly accurate, and not overestimated, as had been feared.

In this connection it is of interest to note that Sir Wm. Crookes[4] has calculated, from certain assumptions, that carbon has zero vapor presure at 3,000° Abs., or approximately 2,700° C., which is about the temperature (estimated from the calibration curve) at which a more rapid wasting of the heater becomes noticeable.

X. Conclusion.

I believe that this furnace opens up a wide field for investigation of high temperature phenomena under exact and easily controlled conditions, and hope that eventually it will enable us to become familiar with the properties of substances up to extremely high temperatures.

I expect soon to be able to give the results of a number of interesting investigations which are now in progress.

Research Laboratory, General Electric Company,
Schenectady, N. Y.

DISCUSSION.

President Bancroft: There was one point that occurred to me while Mr. Arsem was showing the lantern slides giving the relation between temperature and energy. If the formula holds accurately, it would be much better to plot these on logarithmic co-ordinates; in that case, we should have a straight line from which, of course, it is much easier to extrapolate, instead of plotting logarithms from this.

Mr. Arsem: It is easier to subdivide the spaces, the way I did it.

Mr. Collens: In reference to the deposit of graphite which Mr. Arsem mentions as forming under certain conditions on the surface of the tube, and which he claims to be deposited carbon vapor, I should like to ask whether this has been analyzed at all for graphic oxide, to prove that it is graphite and not

[4] Proc. Roy. Soc. A 76,458 (1905.)

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some form of amorphous carbon. The deposit on the sample tube which has been passed around is the color of graphite, but lacks many characteristics of graphite. It seems hard and brittle, and does not leave a mark when rubbed with the finger.

MR. CARL HERING: I understand that the crucible cannot be taken out while hot, in order to cast the materials; they have to be allowed to cool in the furnace. Is this correct?

MR. ARSEM: You can cast them; I have cast certain alloys; but we have not desired to cast them, that is the only reason we have not done it. I have a furnace designed in which I think it is possible to cast an ingot in vacuum in any shape.

PRESIDENT BANCROFT: That is the furnace that we want.

DR. J. W. RICHARDS: It is exceedingly interesting to know this vaporizing point of carbon—2,700° in a vacuum. I would like to caution any one reading this paper, however, not to mix these boiling points or vaporizing points with the ordinary ones. There has been published within the last year, a paper on the boiling points of the metals, in which boiling points of the metals were given as first determined; that is, the first temperature at which there is any sensible vapor tension; and for all practical purposes, these are entirely different from the boiling points under atmospheric tensions, since the phenomena of boiling water under atmospheric tension does not occur at anything like the temperatures at which you get the vaporization in the vacuum. I think it would be very interesting, and would add very much to the value of the paper, if there were published with the paper, the experimental data which have been obtained in regard to the melting points of oxides.

MR. ARSEM: A great many interesting results were obtained, which I hope to publish later.

PRESIDENT BANCROFT: I think we may well be thankful that we got a description of a furnace that will enable us to do the things that this furnace will do; and if necessary, I think we might wait patiently until we are allowed to hear of certain results that may be obtained with it.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

ELECTROLYTIC CORROSION OF THE BRONZES.

By B. E. CURRY.

It is well known that many of our useful metals and alloys are materially affected by corroding agents. Iron rusts in the air, steam pipes corrode and leak, the brass commonly known as Muntz metal dissolves in sea water. Some of the metals form protecting films that prevent further action. Beyond the formation of a thin gray film, tin does not rust; the same is true of aluminum and some other metals. At the present time the corrosion of alloys has been studied but little. It is known that certain brasses dissolve in the same ratio as the copper and zinc present, while other brasses dissolve differently.

Many of the other properties of the useful alloys have been studied in detail, and it is the purpose of this research to study the corroding effects of some of the more common re-agents on the copper-tin series of alloys. The equilibrium diagram has been determined by Shepherd and Blough, and the tensile strength[1] tests have already been published.

The work of Shepherd and Blough has shown that five solid phases occur in bronzes annealed between 200° and 400°. From 100% to 87% copper we have a series of solid solutions known as the α crystals. From 87% to 74.5% the alloys consist of mixtures of A and δ crystals in varying proportions. From 74.5% to 67% we have the δ crystals, a series of solid solutions. These are the crystals which Heycock and Neville believed to be the compound Cu_4Sn. Between 67% and 61.3% we have mixtures of δ crystals with the compound Cu_3Sn, this latter occurring pure at 61.3% copper. Cu_3Sn and the ϵ crystals coexist from 61.3% to 41%. from 41% to 40% we have a new series of solutions, the ϵ crystals. Pure tin and ϵ crystals coexist between 40% and 0% copper.

[1] Shepherd and Upton, Jour. Phys. Chem., 9, 441 (1905).

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The test-pieces were made from very pure electrolytic copper and 99.99% tin, the alloys were melted in Acheson graphite crucibles and cast in cylindrical graphite moulds. They were 8.5 centimeters long and 0.8 centimeter in diameter. The copper was always melted first in the presence of powdered graphite and illuminating gas. After complete fusion of the copper, the tin was added, the melt stirred thoroughly, and then poured. Any bronze may be obtained by this method. The test-piece should be removed from the mould and quenched as soon as sufficiently cold to permit handling. After quenching, the ingots were annealed. The annealing process was carried on in a nickel wire resistance furnace. The process is at an end when equilibrium is reached, as shown by the microscopic examination. After a little experience it is easy to tell fairly accurately, even without the microscope, how long a given alloy should be annealed. All bronzes annealed above 500° must be quenched rapidly in order to prevent the formation of the phases stable at lower temperatures.

After annealing, the test-pieces were cleaned and all traces of oxide removed by means of a file or carborundum paper. Each piece was then numbered and weighed.

In order to make the results more comparable and to save time, the electrolytic tests were run in series. An apparatus was so arranged that five tests could be carried on simultaneously, the same current passing through each test piece as anode. Platinum wire was used for cathodes.

Each test-piece was mounted on the shaft piece of a small Ajax motor by means of a large brass connector. The motors were used only as bearings, and each was driven separately by a belt from a shaft which was connected to a large motor. This arrangement permitted a uniform rate of motion for each test-piece. When once adjusted, the test-pieces were rotated rapidly and steadily. In this way each solution was kept well stirred and uniform throughout. Without effective stirring, uniform results cannot be hoped for.

Test-pieces of the following percentage composition of copper were made: 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 25, 15, 5. This series is sufficiently complete for our purpose. Hereafter, all percentages are referred to copper unless otherwise stated.

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The effect of electrolytic corrosions was examined in solutions of sodium sulphate, sodium nitrate, sodium acetate, alkaline sodium tartrate, acid ammonium oxalate, sodium chloride and copper sulphate.

Tests on chemical corrosions were made by bubbling air through solutions of sodium persulphate, alkaline sodium persulphate, and sodium chloride.

At the end of each test, the bronze was removed from the solution and carefully cleaned with a rubber-tipped stirring rod. All wasn water was added to the original solution. In most cases a very satisfactory cleaning may be secured by a few minutes of patient work. After being cleaned and dried, each piece was heated in a stream of hydrogen until all oxides were reduced. The amount of corrosion may then be determined by reweighing the test-piece, and subtracting this weight from the original weight.

All electrolytic tests were carried on in special thick-walled 250 cc. beakers. About 200 cc. solution was employed for each test. After the test-piece was removed and cleaned, the solution was acidified with nitric acid. The copper was precipitated electrolytically and weighed. If the copper deposit was not bright, or was found to contain tin, it was reprecipitated and reweighed. The tin was determined by difference. Knowing the percentage of copper in the corrosion products and in the original alloy, it was known whether the alloy was becoming tin-rich or copper-rich as a result of the corrosion.

In most tests 7% solutions were used. These were found to be more satisfactory than the more concentrated solutions where the salt crystallizes and creeps over the edge of the beaker.

Neutral solutions were chosen because they could be kept almost uniform, and at the same time the introduction of soluble copper and tin salts was prevented. In the neutral solutions these salts were precipitated as hydroxides the instant they were formed. In neutral solutions the tendency of the dissolved copper to reprecipitate on the test-piece is obviated. It is difficult to prevent the reprecipitation of copper from acid solutions. The same is true for soluble copper salts in alkaline solutions.

Ordinarily the tests were made at room temperature which was subject only to slight variation.

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In all tests, a surface of about 13.8 cm^2 was exposed to solution. In the electrolytic tests a current of about 25 milli-amperes was used. This gives a current density of 0.18 amp/dm^2. The time for each run was about eight hours.

ELECTROLYTIC CORROSION IN SULPHATE SOLUTIONS.

A 7% solution of sodium sulphate was employed for this series of tests. The results obtained in the sulphate solutions are given in table I which, as all subsequent tables, is arranged as follows: The first column gives the composition of the test-piece in percentage of copper; the second the amount of corrosion; the third the amount of copper in the corrosion product; the fourth the percentage of copper in the corrosion product. In this series of tests the α and δ bronzes were annealed at 400°; the Cu_3Sn and ϵ were annealed at 217°.

TABLE I.

7% Sodium Sulphate Solution.

Percentage of copper in test piece.	Corrosion in grams.	Grams copper corroded.	Percentage of copper corroded.
95	0.3787	0.3638	96.07
90	0.3617	0.3411	94.3
85	0.1289	0 1245	97.3
80	0.0850	0.0812	95.6
75	0.0416	0.0400	96.1
70	0.0070	0.0060	
65	0.0061	0.0036	
60	0.0041	0.0030	
55	0.0037	0.0030	
50	0.0052	0 0040	
45	0.0049	0.0039	
40	0 0015	0.0009	
35	0.0410	0.0126	30.1
25	0.1579	0.0213	13.3
15	0.2629	0.0224	8.5
5	0.3707	0.0121	3.2

There is no apparent difference in the way in which the 95% and 90% bronzes dissolve. In a given time with the same current, both solutions contain about the same bulk of oxides. The solubility of the 85%, 80% and 75% bronzes is much less, and decreases very rapidly in the order named. There is a very marked tendency for these to become passive. The 70% bronze is prac-

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tically insoluble. The bronzes between 70% and 40% do not dissolve in sulphate solutions. With less than 40 % copper content all of the bronzes corrode in sulphate solutions. The 35% bronze dissolves only slightly (the dissolved portion is almost pure tin), and the amount of corrosion increases as the copper content decreases. All these changes can be detected in a rough way by the appearance of the electrolyte as the action continues.

The corroding action does not change the appearance of the 95% bronze except for a slight tendency to become tin-rich on the surface. The 90% bronze becomes tin-rich as the action continues; this tendency is slight, but more marked than in the 95% bronze.

The 85%, 80%, 75%, 70%, bronzes become decidedly tin-rich. The surfaces of the 85%, 80% and 75% have the appearance of metallic tin. The 65%, 60%, 55%, 50%, 45%, 40% bronzes dissolve so slightly that there is no apparent change. All bronzes with less than 40% copper content become copper-rich on the surface. There is not a marked tendency for the copper-rich, or α bronzes, to become passive. The α crystals dissolve almost without change. The 95% and 90% bronzes are composed of pure α crystals. The 85%, 80% and 75% bronzes are composed of a mixture of the two phases α and δ. These latter form a protecting film on the surface which tends to make the bronze passive. Because of the presence of the soluble α phase, the film is porous, and the corrosion continues but at much reduced rate. The 74% bronze is composed of homogeneous δ crystals. The protecting film formed on this bronze is only slightly porous and very effective. The film on the δ bronzes is tin-rich and easily detected.

The bronzes between 74% and 40% copper content form a very thin invisible film on the surface. Its presence can be detected when the bronze is heated in a hydrogen atmosphere. There is always a slight loss in weight when so treated.

All bronzes with less than 40% copper content have the phases E and pure tin in equilibrium. The ϵ phase becomes passive, and the tin dissolves. The solubility increases as the ϵ phase decreases in amount. The 35% bronze dissolves slightly, while the 5% bronze dissolves very readily. There is a tendency for these bronzes to disintegrate as the corrosion continues. Tin is dissolved

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from around the E crystals, and these finally fall into the solution but do not dissolve.

The first results obtained in the sulphate solutions were puzzling for a time. The amount of copper in the corrosion product was often greater than the anode loss. The methods of analysis were checked and found to be correct. The anodes were then reduced in hydrogen, and in the process lost considerable weight. This explained the difficulty, and at the same time showed that the protecting film was some form of oxide. At first sight the film has the appearance of metallic tin.

In Fig. 1 is shown the efficiency curve for the series of tests. This curve is not absolute, but represents the facts in hand. The data were obtained in part by extrapolation, and are not given here.

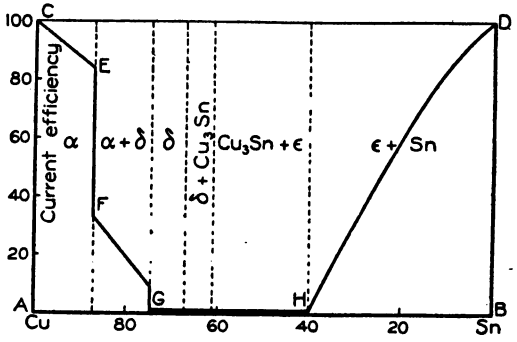

Fig. 1.

The horizontal line AB represents the concentration of copper and tin with the pure components at A and B respectively. The current efficiency is represented vertically from the line AB with 100% efficiency at C and D for the pure copper and tin, copper being considered as bivalent, and tin as quadrivalent. All other efficiency curves are presented in this way except that copper is considered as univalent, and tin as bivalent in chloride solutions. To bring out the relation between corrosion and composition more clearly, the fields for all the phases except pure ϵ are indicated by means of dotted lines.

The efficiency curve consists of four branches. The branch CE represents the efficiency for the α bronzes; FG for the $\alpha + \delta$

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bronzes; GH for the δ, δ + Cu_3Sn, and Cu_3Sn + E bronzes; and HD for the ϵ + Sn bronzes. These are very distinct branches, and conform very closely to the equilibrium diagram. The efficiency for δ Cu_3Sn, and ϵ bronzes is almost zero, and the curve is almost flat over this range. The two soluble phases are α and tin. When either of these is in equilibrium with an insoluble phase the efficiency drops very rapidly.

From the nature of the corrosion of the ϵ and Sn bronzes it was evident that almost no ϵ was dissolved. Accordingly, a short run was made on these. Care was taken to remove any undissolved ϵ crystals from the solution before proceeding with the analysis. The results are recorded in Table II.

TABLE II.

7% Sodium Sulphate Solution.

Copper in test-piece.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
35	0.0390	0.0007	1.7
25	0.0985	0.0004	0.4
15	0.1967	0.0007	0.4
5	0.1058	0.0020	1.9

Practically, the ϵ does not dissolve at all, and the corrosion product is pure tin. The high copper content found in the corrosion product for the ϵ and Sn bronzes recorded in Table I, is due to the fact that the entire corrosion product was dissolved before analyzing for copper. Even there the copper content is much lower than in the test-piece.

ELECTROLYTIC CORROSION IN NITRATE SOLUTIONS.

For this series of tests, a 7% solution of sodium nitrate was used.

The α and Sn bronzes were annealed at 400° C., and the Cu_3Sn and ϵ at 217° C.

The results are recorded in Table III.

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TABLE III.

7% Sodium Nitrate Solution.

Percentage copper in test-pieces.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
95	0.2528	0.2452	97.0
90	0 2593	0.2386	92.0
85	0.2513	0.2471	98.2
80	0.2555	0.2386	93.0
75	0.1142	0.1000	87.5
70	0.0507	0.0415	81.8
65	0.0049	0.0038	
60	0.0087	0.0061	
55	0 0037	0.0024	
50	0.0040	0.0032	
45	0.0027	0.0032	
40	0.0045	0.0043	
35	0.0491	0.0077	15.7
25	1.7904	0.3783	21.7
15	1.2990	0.1824	14.0
5	1.0752	0.0433	4.3

The behavior of the bronzes is similar to that in the sulphate solutions. The α bronzes dissolve readily, and tend to become tin-rich on the surface, but only very slightly. The $\alpha + \delta$, and δ bronzes become decidedly tin-rich on the surface. The protecting film has little effect on the bronzes poor in δ. This is most likely due to its porosity. The 75% bronze which is almost pure δ, forms a protecting film which is fairly stable. The δ, $\delta + Cu_3Sn$, $Cu_3Sn + \epsilon$ and ϵ bronzes are insoluble. These form a very thin protecting film which does not break down in nitrate solutions. The bronzes with less than 40% copper content corrode in nitrate solutions. The amount of corrosion is slight where the bronze is nearly pure ϵ, but increases as the bronzes approach pure tin. This is due to the fact that the ϵ crystals are not soluble as compared to pure tin. The tin soon disappears, and forms a bronze rich in the ϵ phase, and the solubility must then decrease.

Ordinarily we would expect tin to dissolve as stannic nitrate in nitrate solutions. This is found to be contrary to fact. When a tin anode is run in series with a copper voltameter, the amount of corrosion is practically 2.5 times that found in the voltameter. We would expect the tin anode to lose practically the same weight as does the copper, or in fact, a little less.

Fig. 2 shows the efficiency curve for this series of tests. The branch C E represents the efficiency for the α and $\alpha + \delta$ bronzes

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This curve is continuous and regular until almost the pure δ bronze is reached. At a composition near 75% the efficiency drops very rapidly and continues very low through the δ bronzes. The sudden drop is seen in the part of the curve E G. Over the range from 70% to 40% copper content, the branch GH is flat. The δ + Cu_3Sn, Cu_3Sn + ε, and ε bronzes, do not dissolve. With less than 40% copper, the corrosion goes on at an abnormal rate as already noted. The 35% bronze dissolves with a low efficiency. With still less copper content the branch HI rises very abruptly and extends to a point representing about 250% for pure tin[2].

Table IV gives the results obtained for a short run in nitrate solutions. Care was taken here to remove the ε crystals from the

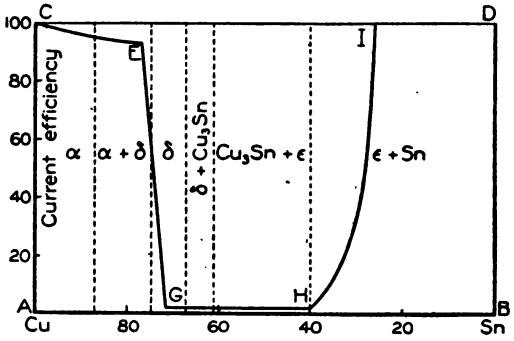

Fig. 2.

solution before analyzing for copper. The analyses show that the ε crystals are not dissolved in the nitrate solutions, but are dislodged when the cementing material, or pure tin, is dissolved away.

TABLE IV.

7% Sodium Nitrate Solution.

Percentage copper in test-piece.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
35	0.0565	0.0008	1.4
25	0.2355	0.0046	1.9
15	0.1463	0.0025	1.6
5	0.2198	0.0013	0.6

[2] It is probable that tin is bivalent when anode in nitrate solution, and that the extra 25 per cent. loss is due to disintegration.

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A series of bronzes of the following composition 85%, 80%, 75%, 70%, 65% were annealed at 625 degrees C, and quenched in water. The phases present in this series are A, β, γ, and Cu_3Sn. On quenching, the 70% bronze broke into many pieces, and its corrosion properties could not be determined. A short piece of the 65% bronze was finally obtained from this temperature. These bronzes were treated in the same manner as the bronzes in the previous tests. The results are given in Table V.

TABLE V.

7% Sodium Nitrate Solution.

Percentage copper in test-piece.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
85	0.3150	0.2950	93 6
80	0.3170	0.2808	91.7
75	0.0581	0.0503	86.5
65	0.0235	0.0220	85.1

The behavior of the β and γ bronzes is not unlike that of δ. The efficiency of the α and β bronzes is practically the same as for $\alpha + \delta$. β dissolves slightly at the beginning but becomes passive very quickly. The 65 % bronze which represents $\gamma + Cu_3Sn$ does not dissolve. The β and γ bronzes are very brittle, and can scarcely be quenched to prevent breaking. All these bronzes become tin-rich on the surface.

The efficiency curve for these bronzes is shown in Fig. 3 by the curve C E G H. The branch CE coincides with the corresponding branch of the curve for the $\alpha + \delta$ bronzes. The branch corresponding to β, $\beta + \gamma$, γ, $\gamma + Cu_3Sn$, is flat.

Since the β and γ bronzes behave in the same way as the δ bronzes in nitrate solutions, they would undoubtedly behave in the same way toward other corroding agents. For this reason and also because of the difficulty of obtaining suitable test-pieces of β and γ bronzes, no further study was made of these.

ELECTROLYTIC CORROSION IN ACETATE SOLUTIONS.

For this series of tests a 7% solution of sodium acetate was employed. The α and δ bronzes were annealed at 400° C, and all others at 217°. The results are given in Table VI.

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TABLE VI.

7% Sodium Acetate Solution.

Percentage copper in test-pieces.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
95	0 0843	0.0826	98.0
90	0.0271	0.0268	98.2
85	0.0073	0.0068	93.1
80	0.0032	0.0034	
75	0.0019	0.0024	
70	0.0023	0.0020	
65	0.0022		
60	0.0013	0.0002	
55	0.0015	0.0016	
50	0.000	0.0005	
45	0.0006		
35	0.0735	0.0020	2.7
25	0.2478	0.0059	2.4
15	0.2251	0.0046	2.4
5	.3233	0.0017	0.5

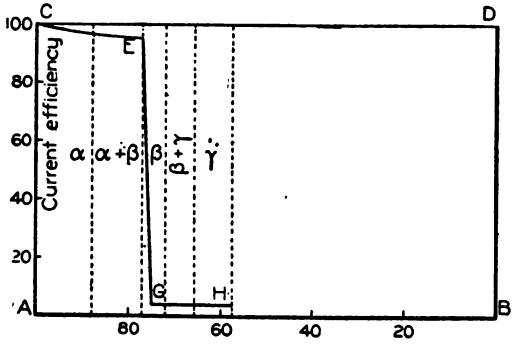

Fig. 3.

Only two phases dissolve in the acetate solutions. The α phase dissolves tin-rich on the surface. An increasing amount of tin in the α bronzes decreases the amount of corrosion rapidly. The δ bronze does not dissolve at all, and its presence prevents the corrosion of the α phase. The 85% bronze corrodes only very slightly. The Cu_3Sn and ϵ bronzes do not corrode at all. With less than 40% copper content the tin dissolves, and the ϵ crystals are left behind. The 35% bronze corrodes only slightly, the free tin content being very low. The amount of corrosion increases as the ϵ content decreases. The 15% bronze corrodes three times as fast as the 35% bronze.

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The efficiency curve for this series is given in Fig. 4. The branch EF represents the efficiency for the α bronze. The branch F G which is almost flat for its entire length represents the efficiency for the $\alpha + \delta$, δ, $\delta + Cu_3Sn$, $Cu_3Sn + \epsilon$, and ϵ bronzes. These do not dissolve at all. The branch G D represents the efficiency for the $\epsilon + Sn$ bronzes.

CORROSION IN CARBONATE SOLUTIONS.

A series of tests were made in a 7% solution of sodium carbonate. The results are given in Table VII.

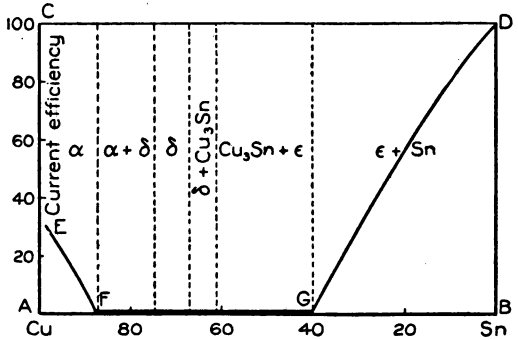

Fig. 4.

TABLE VII.

7% Sodium Carbonate Solution.

Percentage copper in test-piece.	Corrosion in grams.	Percentage copper in test-piece.	Corrosion in grams.
95	0.0021	55	0.0039
90	0.0029	50	
85	0.0030	45	0.0050
80	0.0031	35	0.0028
75	0.0040	25	0 0086
70	0.0039	15	
65		5	0.0019
60			

The bronzes do not corrode in carbonate solutions. The loss in weight at the anode was only very slight at the end of a 7 hour run. It is quite evident that the green carbonate that forms on the surface of bronze exposed to the air, must first dissolve as some other salt which is afterwards changed to a carbonate.

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CORROSION IN ALKALINE TARTRATE SOLUTIONS.

For this series, a solution of 7% sodium tartrate and 5% caustic soda was used. The results are given in Table VIII.

TABLE VIII.

7% Sodium Tartrate Solution + 5% Caustic Soda.

Percentage copper in test-pieces.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
95	0.2770	0.2610	94.3
90	0 2628	0.2373	90.3
85	0.2551	0.2206	86 5
80	0.2474	0.1976	80.3
75	0.2353	0.1767	75.1
70	0.2300	0.1598	69.5
65	0.1380	0.0877	64.3
60	0.1200	0.0727	60.2
55	0.0767	0.0427	55.6
50	0 0550	0.0284	51.6
45	0 0600	0.0241	46.3
35	0 3501	0.0755	21.6
25	0.4809	0.0321	6.8
15	0.5607	0 0296	5 2
5	0.5383	0.0073	1.4

All bronzes corrode in alkaline tartrate solutions. The α and δ bronzes dissolve without change. The $\alpha + \delta$ bronzes undergo a slight change. The α phase dissolves first, and leaves a surface richer in δ crystals. After this shift takes place, the solution continues without further change, and the corrosion product has the same composition as the bronze.. This shift is slight, and is not easily detected by analysis when the amount of corrosion is great. The $\alpha + \delta$ bronzes become tin-rich on the surface. The appearance of the α and δ bronzes is little changed. The appearance of the $\delta + Cu_3Sn$, $Cu_3Sn + \epsilon$, and ϵ bronzes is not changed by corrosion. The corrosion product has the same composition as the bronze. The $\epsilon + Sn$ bronzes become copper-rich on the surface. The free tin dissolves first, and the ϵ crystals are left behind. However, the ϵ crystals are broken down to a certain extent, and a considerable amount of copper is found in solution, but this is always much less than the copper content of the bronze.

The bronzes do not form a protecting film in the alkaline tar-

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trate solutions, and the corroded bronzes do not lose weight when heated in hydrogen.

The efficiency curve is shown in Fig. 5. This curve consists of three branches. The branch C E represents the efficiency for the α, $\alpha + \delta$ and δ bronzes. The branch FG represents the efficiency for the $\delta + Cu_3Sn$ and $Cu_3Sn + \epsilon$ bronzes. The Cu_3Sn is less soluble than the δ, and the efficiency drops for these bronzes. The ϵ is less soluble than the Cu_3Sn, and the efficiency drops to a minimum at a 40% copper content for pure ϵ. The branch CD represents the efficiency for the ϵ and Sn bronzes.

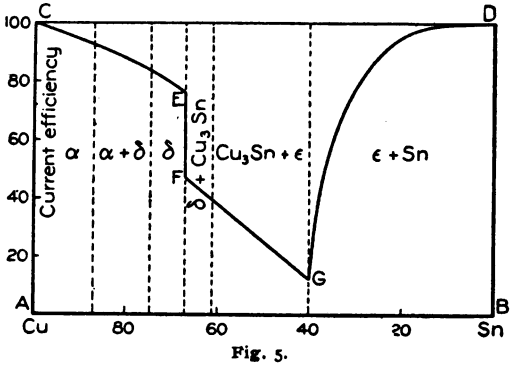

Fig. 5.

ELECTROLYTIC CORROSION IN ACID OXALATE SOLUTIONS.

For this series of tests, a solution containing 3% ammonium oxalate and 3% oxalic acid was used. The results are given in Table IX.

TABLE IX.

3% Ammonium Oxalate Solution + 3% Oxalic Acid.

Percentage of copper in test-pieces.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
90	.231	.2086	90 1
85	.2390	.2037	85.2
80	.2432	.1948	80.1
75	.2416	.1819	75.3
70	.2531	.1772	70.1
60	.1820	.1102	60.5
50	.1263	.0644	51.0
40	.0659	.0255	38.6
15	0.4349	.0044	1.0

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All bronzes corrode in acid oxalate solutions. In general, the behavior is exactly the same as in the alkaline tartrate solutions.

The anodes remain perfectly clean and bright throughout the run, and do not lose weight when heated in hydrogen. There is but slight tendency for the α and δ bronzes to go tin-rich. The efficiency curve is shown in Fig. 6. The curve is not completed for the ϵ + Sn bronzes, but for these the tin and some ϵ dissolve. The α, and α + δ bronzes give practically 100% efficiency in this solution. The curve has a minimum at 40% copper content, or for the ϵ bronze.

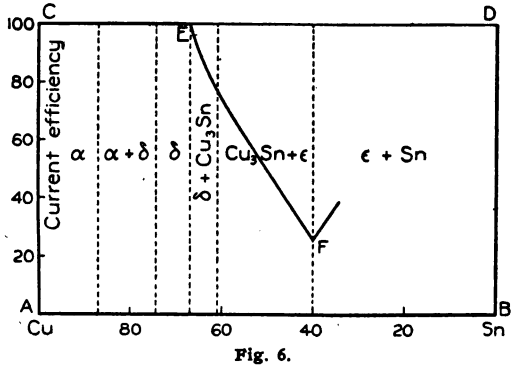

Fig. 6.

ELECTROLYTIC CORROSION IN CHLORIDE SOLUTION.

The chloride tests were run in a 7% solution of sodium chloride. The results are given in Table X.

TABLE X.

7% Sodium Chloride Solution.

Percentage copper in test-pieces.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
95	0.3486	0.3318	94.9
90	.3478	0.3135	90.1
85	.3216	0.2775	86 3
80	.3282	0.2693	82.1
75	.2793	0.2106	75 4
70	.2416	0.1701	70 4
65	.2462	0.1611	65.4
60	.2537	0.1538	60.3
55	.2598	0.1402	54.0
50	.2736	0.1363	49.8
45	.4021	0.1802	44.8
35	.3693	0.0525	14.2
25	.3051	0.0584	19.1
15	.4425	0.0448	10.1
5	.4237	0.0169	3.83

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In chloride solutions the α bronzes dissolve without change, while the α and δ bronzes become tin-rich on the surface. The α phase dissolves first, and leaves a surface rich in δ. After this shift takes place the bronze continues to dissolve without further change. The δ, $\delta + Cu_3Sn$, $Cu_3Sn + \epsilon$ bronzes undergo very little change if any. The $\epsilon + Sn$ bronzes go copper-rich on the surface because the tin dissolves and leaves the ϵ phase.

The chloride solutions are the most difficult of any to deal with. The copper and tin dissolve as cuprous and stannous chlorides; basic salts form, and the solution becomes alkaline. Unless the alkalinity is kept down by the addition of acid, a thick adherent scale forms on the test-piece. In an alkaline solution, the tin is removed from this scale, and it becomes rich in copper. When

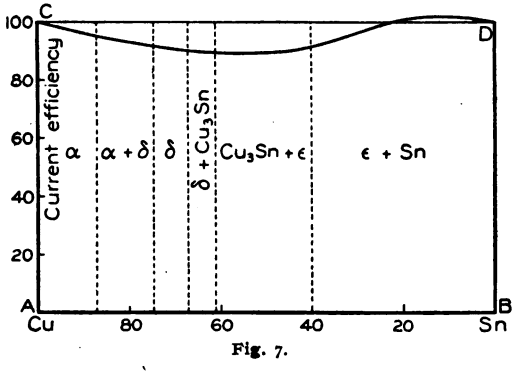

Fig. 7.

cleaning the test-piece, before reduction in hydrogen, all chlorides should be removed, otherwise both copper and tin are distilled off.

The bronzes do not become passive in chloride solutions. An 80% bronze was made anode in a sulphate solution until well coated with the protecting film. The piece was then transferred to a chloride solution where it began to dissolve immediately.

The efficiency curve for this series is given in Fig. 7. The curve is continuous, has no marked irregularities, and approximates the theoretical values.

In Table XI are recorded the results of a run in sodium chloride in which the solution became alkaline and remained so. The adherent crust of oxides was not removed. At the end of the

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run, the test-pieces were removed and washed, but not scraped in any way. When dried, each piece was reduced in hydrogen and weighed. It is at once evident from the analysis that the scale was copper-rich. The tin had been removed from the mass of precipitated hydroxids, and the copper left behind. In the reduction of the unremoved scale some tin and a little copper were lost by distillation. But aside from this, the analyses show the effects of the alkaline solution. The scale is a corrosion product, and may be removed. When this is done, the new surface is not different from the original, and the corrosion product and the test-piece have the same composition.

TABLE XI.

7% Sodium Chloride Solution.

Percentage copper in test-piece.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
75	0.0968	0.0655	67.6
70	0.1077	0.0609	56 4
65	0.1103	0.0642	58.2
60	0.1014	0.0468	45.1
55	0.1182	0.0561	47.4
50	0.1123	0.0372	33.1
40	0.1809	0.0402	22.2
35	0.1380	0 0207	15.0
25	0.1598	0.0171	10.7
15	0.1395	0.0020	1.4
5	0.1541	0.0020	1.3

In order to compare the effects of chemical corrosion with those of electrolytic corrosion, some measurements were made in sodium persulphate solutions without bubbling air in, and in sodium chloride solutions through which a continuous stream of air passed. It was expected that the sodium persulphate solutions would give results comparable with those obtained by the electrolysis of sodium sulphate solution. It was also hoped that the corrosion by air in presence of sodium chloride would be similar in nature to the electrolytic corrosion in sodium chloride solutions. The analogy is not absolute. The chemical corrosion would be identical with the electrolytic corrosion if we had bubbled chlorine into the solution. As no one cares how the bronzes corrode in presence of chlorine, this experiment was not tried.

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On the other hand, oxygen, as an oxidizing agent, stands between chlorine and bromine, and the apparent differences are due to the possibility of passivity in presence of oxygen. Since metals do not become passive in chloride solutions, it was thought probable that the electrolysis of chloride solutions would give a fairly accurate measure of the corrosion by air in chloride solutions.

CHEMICAL CORROSION IN SODIUM PERSULPHATE SOLUTIONS.

For this series of tests, a 20% solution of sodium persulphate was used. The test-pieces were allowed to stand in the solutions for sixteen days. The results are given in Table XII.

TABLE XII.

20% Sodium Persulphate Solution.

Percentage copper in test-piece.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
95	4.1613	3.9490	94.9
90	0.6269	0.5645	90.2
80	0.2748	0.2617	95.2
65	0.0664	0.0620	93.3
50	0.0085	0.0060	70.5
25	0.1256	0.0098	7.8

The α bronzes dissolve without change in persulphate solutions. The $\alpha + \delta$ bronzes become tin-rich on the surface. The α phase dissolves first, and leaves the tin-rich δ phase behind. The δ, $\delta + Cu_3Sn$, $Cu_3Sn + \epsilon$, and ϵ bronzes do not corrode rapidly in persulphate solutions. These become passive, and little further solution takes place. The $\epsilon + Sn$ bronzes corrode, and go copper-rich on the surface; the pure tin dissolves first, and the ϵ crystals are left.

In persulphate solutions, the soluble phases are α and tin. The 95% test-piece was dug out in deep holes, the surface remained very bright and free from adherent oxides. The appearance of the 90% piece was less changed. The surface was less pitted, and the amount of corrosion much less. The 85% and 65% pieces were tin-rich on the surface. The 65% and 50% pieces were coated with an oxide, and were only slightly corroded. The 25% pieces were pitted, and the slime contained undissolved ϵ crystals.

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CHEMICAL CORROSION IN ALKALINE PERSULPHATE SOLUTIONS.

For this series, a 20% solution of sodium persulphate was made strongly alkaline with caustic soda. The test-pieces were allowed to stand in the solutions for sixteen days. The data are given in Table XIII.

TABLE XIII.

20% Sodium Persulphate Solution + Excess Caustic Soda.

Percentage copper in test-piece.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
95	2.4075	2.3038	95.2
90	1.5424	1.3924	90.3
80	0.0829	0.0746	90.0
65	0.0063	0.0047	74.6
25	1.6478	0.2558	15.5

In alkaline persulphate solutions, the α bronzes dissolve without change. The α and δ bronzes go tin-rich on the surface. The pure δ, $\delta + Cu_3Sn$, $Cu_3Sn + \epsilon$ bronzes are only slightly corroded. The ϵ +Sn bronzes become copper-rich. The corrosion product contains ϵ crystals intact. The bronzes examined behave in the same way toward both the neutral and alkaline persulphate solutions. The behavior here is not different from that in the electrolytic tests with sodium sulphate solutions.

CHEMICAL CORROSION IN SODIUM CHLORIDE SOLUTION.

In this series of tests a 7% solution of sodium chloride was used and air was bubbled through the solution continuously. In this way oxygen was supplied and at the same time the solution was kept well stirred. The following bronzes were examined: 95%, 85%, 70%, 65%, 60%, 50%, and 25%. The results are given in Table XIV.

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TABLE XIV.

7% Sodium Chloride Solution.

Percentage of copper in test-piece.	Corrosion in grams.	Grams copper corroded.	Percentage copper corroded.
95	.0954	.0916	96.0
85	.0534	.0480	88.2
70	.0563	.0390	69.4
65	.0450	.0296	65.8
60	.0400	.0240	60.2
50	.0430	.0129	51.0
25	.0360	.0022	6.0

The α bronzes dissolve without change and fairly rapidly. The $\alpha + \delta$ bronzes dissolve less rapidly and become tin-rich on the surface. The α crystals dissolve first and leave the surface rich in δ crystals. The δ, $\delta + Cu_3Sn$, $Cu_3Sn + \epsilon$, and ϵ bronzes corrode very slowly and undergo very little change if any during the process. The ϵ + Sn bronzes become copper-rich, the Sn dissolving first.

In this experiment the 95%, 85% and 25% pieces were subjected to the action of the salt solution and oxygen for five weeks. The others were allowed to run nine weeks. It is at once evident that the action goes on very slowly especially where the δ, Cu_3Sn, and ϵ bronzes are involved. While the α bronzes corrode very appreciably, a single determination necessitates much time.

The observations made on chemical corrosion conform very closely to those made in the electrolytic way. For this reason and also because of the great amount of time involved, a more thorough study of the chemical effects was not made. However, we are of the opinion that a more extensive study would only prove more conclusively that the same general results may be obtained in much less time by the electrolytic method. By shortening the time factor from two months to one day the process may be observed more closely and the introduction of undesirable factors prevented.

ELECTROLYTIC CORROSION IN MISCELLANEOUS SOLUTIONS.

To determine the effect, if any, of an ammonium salt, test-pieces of 85% and 75% copper content were run in series in 7% solutions of ammonium sulphate. The 85% piece lost 0.2351 gram

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in weight, and the 75% lost 0.0130 gram. The corrosion product from the 85% bronze was 98% copper, and from the 75% bronze 90% copper. The electrolytic corrosion with ammonium sulphate is therefore practically the same as with sodium sulphate. The next experiment was made to find out whether the presence of a copper salt in solution would check the dissolving of copper from the anode.

The 75% and 65% bronzes were run in series in a 7% solution of copper sulphate. The 75% piece lost 0.0174 gram, and the 65% piece lost 0.0055 gram. Both went decidedly tin-rich on the surface. The corrosion product was not analyzed. The electrolytic corrosion in a solution containing copper sulphate is practically the same for the copper-rich bronzes as the electrolytic corrosion in sodium sulphate solution.

To show the effect of temperature, a 60% bronze was made anode in a sodium sulphate solution for two hours in a temperature of 80 degrees C with a current of 0.025 ampere; the anode loss was 0.025 gram. This difference of temperature is not sufficient to change the effectiveness of the protecting film.

ANALYSIS OF THE PROTECTING FILM.

Both tin and copper dissolve quantitatively when made anode in salt solutions. The bronzes do not dissolve quantitatively. The film which forms on these bronzes causes the efficiency to drop. This film is apparently tin-rich, and when the corrosion has proceeded far enough, the film may be removed in quantities. A few grams of this film were obtained for analyses. After reduction to the metallic condition, the copper content was found to be nearly 20%, but this was subject to variation. As some or perhaps all of this copper might have been retained mechanically, a different method was tried.

Another portion of the film was placed in a platinum crucible, and a solution of sodium sulphate added. The crucible was made anode, and the solution electrolyzed. The gray powder broke down, and very nearly pure stannic oxide remained undissolved. This insoluble residue was analyzed, and found to contain less than 1 % copper. If this film were a compound, there is no evident reason why it should have broken down under these conditions.

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This evidence points to the conclusion that the film is stannic oxide with more or less occluded copper. The film for these tests was obtained from an 80% bronze. Attempts to form a compound from the oxides of copper and tin in a fused bath, were without success. The film is formed electrolytically only in solutions in which stannic oxide would be stable. It is not known why certain alloys should give it and others not, and it is also not known why there is a formation of a film rather than of a powder.

In connection with these corrosion experiments we found that the pure block tin water pipes in the laboratory were badly corroded. The gray surface film which forms under ordinary conditions had broken down and the pipes were coated with a white powder similar to stannic oxide in appearance. Portions of this corrosion product were removed and examined for the presence of the common laboratory acids. Sulphates, chlorides and nitrates were found to be present in quantities. In other laboratories where acids were used to a less extent, the tin pipes were less corroded. In laboratories where almost no acids were used the pipes were normal in appearance and showed almost no evidence of corrosion.

From these observations it is evident that the protecting film found on pure tin surfaces breaks down in the presence of the stronger acids and that corrosion then takes place more rapidly. In air or in the presence of oxygen and CO_2 this film is stable and almost no corrosion takes place. The electrolytic observations on pure tin are very similar to those obtained chemically. Pure tin corrodes very readily in sulphate, chloride and nitrate solutions when treated electrolytically but almost no corrosion takes place in the carbonate solution.

The corrosion results show the impracticability of the solution method for providing the existence of metallic compounds. When a two-phase alloy is dissolved, it must go into solution unchanged or one phase will dissolve faster than the other.

In the case of the A and δ alloys it has been shown that the A phase dissolves first and that the δ phase is left behind. When the residue is analyzed it is found to be richer in tin than the original alloy. Its composition is something near 75% copper and this points to the existence of the compound Cu_4Sn. However, the range of concentration over which δ crystallizes pure varies from 67% to 74% copper.

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Almost pure tin dissolves from the ϵ and Sn bronzes and the residue consists of almost pure ϵ crystals which show about 40% copper when analyzed. This indicates the compound CuSn. It is now certain from the microscopical examination of the annealed alloys that ϵ crystallizes pure over a range of two per cent.

Heycock and Neville[8] worked on these particular cases but their very careful work failed to establish the exact equilibrium relations. Their evidence pointed to the existence of Cu_4Sn and of CuSn, neither of which exist. Solid solutions may form a very insoluble phase which may be easily mistaken for a compound. Unless the solubility observations are supplemented by other evidence the conclusions may be in error.

SUMMARY.

In this research the following results have been obtained:

The electrolytic corrosion effects have been determined in some of the more common salt solutions.

The electrolytic results have been checked by straight chemical tests and the two have been found to agree closely.

The α bronzes corrode more rapidly than any others. In all solutions and by all methods these undergo but little change in the process.

The $A + \delta$ and $\alpha + \beta$ bronzes corrode tin-rich on the surface.

The β, δ, $\beta + \gamma$, $\delta + Cu_3Sn$, $Cu_3Sn + \epsilon$ and ϵ bronzes undergo little change and tend to become passive.

The E + Sn bronzes corrode copper-rich on the surface and tend to disintegrate as the tin dissolves.

The cause for certain of the bronzes becoming passive has been found to be the formation of a film of stannic oxide. This film has been obtained in quantities and its composition determined.

The E bronze withstands corroding action better than any other.

No bronze becomes passive in chloride solutions.

The efficiency curves have been presented for a number of solutions.

A change in the rate of corrosion occurs only at the appearance or disappearance of a phase in the equilibrium diagram.

[8] Phil. Trans., *202 A*, 1 (1904).

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Quantitative relations have been established throughout the work.

This work has been done under the direction of Prof. Bancroft to whom the author is much indebted for kindly advice and criticism.

The expenses of this research have been covered by a grant from the Carnegie Institution of Washington, D. C.

Cornell University.

DISCUSSION.

MR. ARSEM: I would like to ask whether the corrosion by electrolysis can always be de depended on to be the same as without electrolysis. One case occurred to me of corroding copper with a sulphate electrolyte, or with dilute sulphuric acid. Of course, the copper dissolves; but I always supposed you could never dissolve copper in dilute sulphuric acid without the aid of a current.

PRESIDENT BANCROFT: You can dissolve copper in dilute sulphuric acid in the presence of air. Of course, in the electrolytic method, if you do not get 100 per cent. efficiency, there is oxygen set free, and that is analogous to the corrosion in a sulphate solution or sulphuric acid solution containing air. If you work with copper in dilute sulphuric acid with the air carefully kept out, I imagine there would be practically no corrosion; and, of course, it would be analogous neither to the corrosion with air in the solution, nor to the electrolytic solution.

MR. ARSEM: There are certain cases in which the solution pressure of the metal is less than that of hydrogen. I thought perhaps there might be some difference of that kind.

PRESIDENT BANCROFT: It would not be safe to generalize from one metal in the voltaic series and to say that in all cases, electrolytic and chemical corrosion will be precisely parallel; but before long, we shall have more complete data. What we should claim now is that all the evidence that there is, is in favor of the two things running exactly parallel.

PROF. W. LASH MILLER: The striking thing about the sodium sulphate diagram is the perpendicular way in which the line

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EF comes down. That means that the slightest trace of the substance Delta has a great effect on the current efficiency. There were two explanations of this suggested by the speaker, but I do not recollect which of them he thought more probable. One was that the presence of a trifle of Delta might render the other constituent passive, and the second was, that perhaps the surface rapidly got very rich in tin. Were any experiments made to decide this? If it was a case of passivity, then the corrosion of a bronze whose composition lies to the left of F ought to be much hindered by touching it with any alloy containing Delta; while if the second explanation holds, scratching the surface during electrolysis ought to increase the current efficiency. Perhaps Mr. Curry has made some observation that would enable us to decide?

PRESIDENT BANCROFT: My own belief is that it is due to the formation of a film of stannic oxide which is very effective in this case from 75 per cent. down to 40 per cent., and less effective above. We have seen no evidence whatsoever of passivity in any case other than the formation of an oxide film.

MR. CURRY: In the field marked Alpha plus Delta in cut 4, there is a slight difference between the percentage composition of the corrosion product and of the bronze. In this field, the Alpha tends to dissolve first, and leaves the surface rich in Delta crystals; then after that change has gone on for a short time, the surface is richer in Delta than it was in the beginning; but the efficiency is not affected by this change. This change in the surface takes place, but the bronzes do not go passive over that range. In the case of the sulphate solution, where the oxide forms, they go passive, and the efficiency drops. It is quite a different thing from having a surface of metal and a surface that is composed of the film.

DR. J. W. RICHARDS: Mr. Curry's remarks point to what I think would be an improvement in the diagram, if there were added two lines showing the proportion of that efficiency which was due to copper and the proportion which was due to tin in the corrosion products. Then it could be seen, in any place where there was a sharp drop, whether it was a drop in the attack on copper or a drop in the attack on tin, and what the composition of the corrosion products was, and they could be compared with the composition of the alloy.

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PRESIDENT BANCROFT: It would have been very nice to have done this; but it was not possible because the proposed curves would have coincided too closely with lines already present in the diagram, and the result would have been confusing.

MR. CURRY: All the data will be included in the paper; that is, the composition of the electrolyte and the composition of the test piece. There is quite a lot of data, and it is too much to show here.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

OBSERVATIONS ON THE CORROSION OF IRON BY ACIDS.

By C. F. Burgess and S. G. Engle.

It is well known that the rate at which iron corrodes or combines chemically with its surrounding medium depends upon various factors, including temperature, pressure, nature of corroding agent as to chemical composition and purity, speed with which the resulting compound is removed from the corroding surface, and the physical and chemical state of the iron itself.

Many features of scientific and technical interest have been pointed out by investigators of this subject, and there has been produced a large mass of scattered and fragmentary information, ranging from the solvent action of various acids on the individual metallographic constituents of iron alloys to the observations of the pickler that the acid which he obtains from one manufacturer is satisfactory while that which he obtains under the same name from another manufacturer is worthless.

It is the purpose to record here the results of a few observations made in connection with a more extensive study of electrolytic iron under a grant from the Carnegie Institution of Washington. These observations deal mainly with the rapidity of solution of several grades of iron in dilute acids.

The corroding mediums employed were normal solutions of sulphuric and hydrochloric acids, distilled water and chemically pure acids being used. The solutions were kept at room temperature (about 22° C.) and during corrosion, additions of acid were made to keep the solutions at a nearly constant content of free acid.

The several grades of iron which were compared included electrolytic iron which had been deposited from a mixed sulphate and chloride solution, the same iron which had been heated to about 1,000° C. and allowed to cool slowly, soft sheet iron, low in carbon, such as is used in the manufacture of transformer

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plates, and which are herein designated as transformer iron, a temper steel, such as is used in the manufacture of knife blades, and an ordinary grade of cast iron. Sample plates were prepared from these materials, each having about 5 square inches of surface area. The surfaces, prior to immersion in the acids, were ground smooth on an emery wheel to give uniformity and freedom from scale and impurity. The samples were weighed and immersed for measured periods in the acid solutions, removed therefrom and dipped into dilute sodium hydrate, rinsed in hot water, dried and weighed.

The specimens were suspended in the solutions by means of a grooved stirrup of hard rubber, and arranged in such manner that the separate plates did not make contact with each other.

TABLE I.

Loss in grams per square inch per hour. Solution-normal H_2SO_4

Hour	1st.	2d.	3d.	4th.	5th.*	6th.
Electrolytic	.0319	.2933	.4029	.4098	.5137	.4805
Electro, heated	.0053	.0162	.0088	.0112	.0063	.0078
Cast iron	.0758	.0947	.0737	.0373	.0335	.0525
Steel	.0163	.0086	.0703	.1181	.1135	.0974
Transformer iron	.0090	.0136	.0028	.0074	.0084	.0081

Hour	7th.	8th.	9th.†	10th.	11th.	Average
Electrolytic	.4284	.4221	. .	. .	. .	.3728
Electro, heated	.0071	.0067	.0084	.0120	.0105	.0091
Cast iron	.0638	.0581	.0668	.0677	.0842	.0643
Steel	.1182	.1371	.1344	.1153	.1396	.0971
Transformer iron	.0097	.0104	.0107	.0112	.0119	.0093

* Added 3. lg. H_2SO_4 per liter to replace that consumed by iron.
† " 4.6 " " " " " " " " " "

Table I shows the relative rates of corrosion of the five samples of iron for successive hours during the progress of the test. The striking facts which are brought out numerically in this table, and graphically in the curves plotted on Plate I are that electrolytic iron in the condition which it possessed just as it was taken from the tanks, corroded at a far greater rate than did the other samples, about six times as rapidly as the cast-iron, four times as rapidly as the steel, and nearly forty times as rapidly as the transformer iron. It is also shown that the heat treatment to which the electrolytic iron was subjected, conferred upon it the property of resisting corrosion to a great degree, the heated electrolytic iron dissolving at a hardly appreciable rate as compared with the samples which had been unheated.

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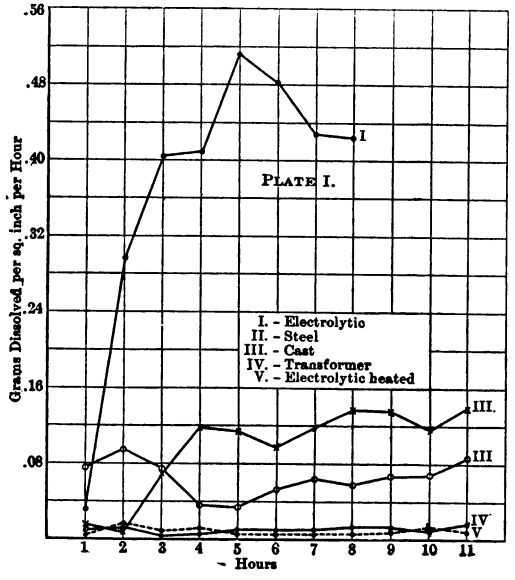
As indicated in the table, the specimen of unheated electrolytic iron was removed from the test at the end of the eighth hour, this having been done on account of its having been practically consumed. That this sample was acted upon far more vigorously than were the others was shown by the rapid evolution of hydrogen which proceeded from it.

In removing the test specimens from the solution at the end of each hour, a certain amount of loosened material became detached, except in the case of the electrolytic samples, which remained smooth and bright; and to avoid any irregularities in



the weight determinations which might result from this, duplicate samples were again placed in normal solutions of the acids and left for seventeen hours without disturbing. As regards rates of corrosion in this test, the various grades of iron held the same relations as they did in the first run, while in the hydrochloric acid, the steel showed the least tendency to dissolve. The results of this run are given in Table II. In this table are given also the rates at which zinc of the grades known as "chemically pure" and "commercial" were dissolved in sulphuric acid.

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TABLE II.

Loss in grams per square inch per hour on a 17 hour run.

	In normal H_2SO_4.	In normal HCl.
Electrolytic	.4575 g.	.2146 g.
Electro, heated	.0209 "	.0083 "
Steel	.0946 "	.0026 "
Cast iron	.0796 "	.1058 "
Transformer iron	.0279 "	.0095 "
Zinc, c. p.	.1410 "	
Zinc, commercial	.2607 "	

It is a well-known fact that pure zinc dissolves in acids much more reluctantly than does the less pure metal, this phenomenon commonly being attributed to the influence of the more numerous galvanic couples which are produced by the larger number of particles of impurity in the latter grade of zinc. Reasoning from this analogy, it would be natural to expect that electrolytic iron, having a high degree of purity, as compared with the other samples, would dissolve at a much slower rate. The striking evidence that this is not the case is shown by the above data and curves, and the remarkable chemical activity of the electrolytic iron calls for explanation. From the fact that electrolytic iron contains considerable quantities of hydrogen, in an occluded or combined condition, it might be suggested that we should look to the influence of this element as the cause of this phenomenon. This view has for its support the observation that upon heating the iron to a red heat, and thus driving off most of the hydrogen, the corrodibility is decreased in a remarkable degree.

It is the belief of the writers, however, that if hydrogen produces an influence, it does so only indirectly, and that the crystalline structure should be taken into account. Electrolytic iron, as deposited from its electrolyte, assumes a marked crystalline structure, as shown plainly not only by the microscope but also to the unaided eye. The nature of this structure, as shown on fracture, varies from needle-and-fern-like forms to a more dense and compact condition, depending upon current density, composition of solution, and other factors. These structures disappear upon heating to a bright yellow heat such as was used to drive off the hydrogen, and an examination by the microscope shows the iron to assume the form which is characteristic of that of

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a pure wrought iron, typical ferrite grains being plainly apparent. Incidentally, it might be noted that this change in structure is accompanied by marked alteration in the physical properties, the iron changing from a hard and extremely brittle condition to a soft, tough state.

To determine whether the crystalline structure of electrolytic iron has an influence on the rate of dissolving in acid solution, two samples were chosen, one of which was coarsely crystalline, deposited from a ferrous ammonium sulphate solution with a small amount of ferrous chloride, and the other deposited from a solution containing a larger percentage of chloride and which gave a much more dense and fibrous deposit. The results are given in Table III.

TABLE III.

Loss in grams per square inch per hour on a 17 hour run. Normal H_2SO_4.	
Electrolytic iron, coarsely crystalline	.4805 g.
Same iron heated	.0685 "
Electrolytic iron, more dense	.3291 "
Same iron heated	.0225 "

At the Bethlehem meeting of the American Electrochemical Society, a paper was presented, dealing with the presence of arsenic in sulphuric acid as influencing the activity of the acid on iron. The various samples herein described were subjected to a normal sulphuric acid solution which contained a small amount of arsenic, and after twenty-two hours, the amount of iron dissolved from all of the specimens was so small as to be undetected, the electrolytic, as well as the other forms of iron, becoming practically passive in the arsenical solution. The explanation which has been offered for this phenomenon is that the iron receives, by contact with the solution, an extremely thin coat of arsenic which resists the action of the acid and protects the underlying metal. While such coating was not detected by the eye, the presence of arsenic was shown by the following test: A strip of pure iron which had become passive by the action of arsenic in sulphuric acid, was removed from the solution and washed in running water for several hours. It was then put into a Marsh's Apparatus and acted upon by a strong solution of arsenic-free sulphuric acid. The gases which were evolved were delivered through a solution of silver nitrate,

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soon producing the characteristic black metallic silver precipitate, caused by the presence of the arsenicuretted hydrogen gas. A similar sample of iron which had not been subjected to the arsenical solution produced no black precipitate.

From the fact that an extremely small amount of arsenic in the presence of iron can enable that iron to resist a corroding influence as strong as that exerted by sulphuric acid, it is natural to infer that this element might be employed in protecting iron from atmospheric and other corroding influences.

In studying the influence of arsenic on steel, Mr. J. E. Stead found[1] that arsenic, instead of being the enemy of the steel maker, as had been commonly assumed, might, in fact, under certain conditions, be his friend, in imparting desirable properties to low carbon steels. Among other observations, he noted that in iron wires containing from .11 per cent. to .21 per cent. of arsenic and carbon from .10 per cent. to .4 per cent., the corrosion by sea water was materially lower than in wires of similar composition, but with lower amounts of arsenic. He says: "Oxidation is retarded by the presence of small quantities of arsenic."

We have not found references to additional work along this line, and in view of the great importance of continued study on the corrosion of iron, and the possibility of using arsenic as a means of imparting greater durability, a further study of the influence of this element seems warranted.

To determine whether electric potentials of iron, with its corroding electrolyte, has any relation to its tendency to corrode, the contact potentials of the various specimens used in this investigation were measured by the use of the normal calomel electrode, the value of which is assumed as —.56-volt. The results of these observations are given in Table IV. The electrolytic iron is placed at the head of the list according to these measurements, as it is also at the head of the list arranged according to the rate of solution. On the other hand, the arrangement of the other samples is not similar, and, consequently, we cannot assume that the single potential is anything more than a rough guide in suggesting tendency to corrode. It is interesting perhaps to note that all the specimens assumed a more electronegative potential in the arsenical solutions than in the others.

[1] Journal of the Iron and Steel Institute *I*, p. 96. (1895).

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TABLE IV.

Single potentials of metals. (Calomel electrode = —.56) at 24° C.

	n. H_2SO_4	n. $FeSO_4$ (neutral)	n. H_2SO_4 (with arsenic)
Electrolytic iron	.0476 volt.	.1164 volt.	—.073 vol
Electrolytic iron heated	.0270 "	.1056 "	—.146 "
Transformer iron . . .	—.0183 "	.1028 "	—.156 "
Cast iron	—.045 "	.0518 "	—.115 "
Steel	—.062 "	.0303 "	—.136 "

CONCLUSIONS.

That the rate at which an acid dissolves iron depends largely upon the elements with which the iron is associated does not need the confirmatory data here given to establish its truth. It is well known that the various metallographic constituents of iron and its alloys resist in differing degrees the attack of acids, and, consequently, different grades of iron show differences of durability.

That the percentage of purity is not the controlling factor is here shown by the observations that the heated and unheated specimens of electrolytic iron, essentially the same as far as chemical composition is concerned, exhibit the widest possible variations in rate of solution.

The crystalline or granular structure of iron seems to influence rates of corrosion in a marked degree.

The rapidity with which unheated electrolytic iron liberates hydrogen in a dilute acid solution suggests a useful application of this material in the production of pure hydrogen by replacing zinc, which is now commonly used. From Table I, it is observed that from equal surfaces of exposed metal, electrolytic iron liberates hydrogen about four times as rapidly as does pure zinc, and twice as rapidly as the commercial grade.

Another advantage in the use of electrolytic iron in hydrogen generation lies in its higher purity and the consequent increased purity of the resulting gas, as compared with that which is obtained from zinc. One pound of iron produces 16 per cent. more hydrogen than does one pound of zinc, and if a sufficient demand for iron for this purpose should arise, it could be supplied at a cost materially less than that of zinc.

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Traces of arsenic are shown to exert such a marked influence in protecting iron from the corroding action of acids that the employment of this element for protection against ordinary corrosion appears worthy of further investigation.

While the measurement of electric potentials of iron against corroding agents seems to afford some indication as to the rapidity with which it will become attacked, it does not seem possible to establish definite relations between electric potentials and corrodibility.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

PRESIDENT BANCROFT: I should like to ask Mr. Burgess, first, what he did in the way of making his iron-arsenic alloy; and secondly, what he actually found. Did he make an iron, covered with arsenic on the surface, or an iron-arsenic alloy all through; and secondly, how did it actually corrode?

PROFESSOR BURGESS: The way we made the arsenic alloy was to take a small ingot of iron, drill a hole in it, plug it up with arsenic, and melt it in an electric furnace. The arsenic alloys very readily with the iron. Cutting test samples from the resulting ingot, we found that on exposure to the atmosphere, the arsenic-containing sample, rusted more rapidly than ordinary iron; that is, the arsenic seems to promote the rusting.

As far as rate of attack by the acids was concerned, some of our arsenical samples showed greater durabilty than did the pure metal. The results are not sufficiently consistent, however, to enable accurate conclusions to be drawn. If arsenic once gets into the attacking acid solution, the iron seems to throw out a thin layer of arsenic or some compound of it on the surface, rendering it almost completely passive.

PRESIDENT BANCROFT: With all due respect, it does not seem to me that that experiment of Mr. Burgess is either convincing or satisfactory. He has got his arsenic all through his iron, and consequently, of course, has at any given point a relatively low percentage of arsenic. It seems to me that the way to do that,

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would be to have a film on the surface of the iron, rich in arsenic. That would be the condition which would be comparable to the results he has already found, and would really lead to some conclusion; whereas, doing the experiment in the form Mr. Burgess has done it, I cannot see any reason why it should have been expected to work out satisfactorily.

MR. CARL HERING: I believe that if a metal is heated in the vapor of arsenic, the arsenic will alloy with the metal. If that is the case, it seems to me that a superficial coating such as has just been mentioned, could readily be made; in such a case, I suppose it would be a regular alloy of iron and arsenic, and not a layer such as is obtained by electrolysis.

I would like to ask Prof. Burgess whether he has any definite proofs that it is occluded hydrogen or alloyed hydrogen that gives this electrolytic iron its peculiar properties? What proof is there that it is hydrogen?

PROF. BURGESS: I don't know that there is any definite proof that it is hydrogen. Hydrogen is present when iron is very brittle; and when the iron becomes soft, it has been found that there is less hydrogen present. That appears to be the only reason we have for believing that the characteristic hardness may be due to hydrogen.

Replying to Dr. Bancroft's suggestion that the arsenic ought to be rather concentrated on the surface of the iron, it becomes concentrated on the surface, where you have arsenic in solution by the fact that the iron throws it out on the surface. If you have an arsenic-iron alloy and the surface becomes corroded, you might look at it in one of two ways: That both the iron and arsenic are dissolved, and the remaining iron in turn will coat itself over with arsenic from the solution; or that only the iron is dissolved out of the mass of metal, leaving a rather concentrated amount of arsenic near the surface.

MR. CURRY: Did you try adding more arsenic to your sulphuric acid to see what effect that would have? If such a small trace of arsenic caused the corrosion to drop off, it seems to me that the addition of more arsenic to the acid ought to give some sort of conclusive result.

PROF. BURGESS: If you can render your iron almost completely passive by a small amount of arsenic, it seems to be quite evident that with a larger amount, it would also be completely passive.

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MR. CURRY: Was it completely passive with the small amount?

PROF. BURGESS: Yes.

MR. CURRY: My question, then, does not apply.

MR. S. S. SADTLER: It seems to me that this matter of electrolytic corrosion might help that problem a little by making up alloys of iron and arsenic and corroding them the way Mr. Curry has done, finding out whether the different concentrations of arsenic and iron showed great differences in the corrosion.

MR. CARL HERING: Would it not be possible to dissolve a piece of this iron, chemically or electrochemically, and to find out in this way whether or not any hydrogen gas comes off. It seems to me that in some such way, it might be definitely found out whether or not it is hydrogen that causes these properties. It seems to me it is a mere assumption to say that it is hydrogen, although it is likely that it is so.

MR. W. C. ARSEM: In regard to the brittleness of electrolytic iron, I have made some experiments. Some electrolytic iron that was made in the laboratory was fused in a vacuum, so that, of course, all the hydrogen was removed. The iron was now no longer brittle, but its mechanical properties were rather poor, On hammering it out a little, it cracked; the same was true in rolling; and no wire of any length could be drawn. This was traced to the presence of iron oxide in the deposit of iron. Oxides are quite often present in electro-deposited metals. By removing this oxide by heating the small strips of iron to the reduction temperature in hydrogen, and then fusing the iron in vacuo, an oxide-free iron was obtained which was very soft and ductile, and could be drawn out into very fine wire. It seems to me that the oxide plays a greater part than the hydrogen.

MR. H. E. PATTEN: Last summer, with reference to this same point, Prof. Burgess had me try to dissolve some electrolytic iron to determine if we could get an excess of hydrogen by dissolving it, and we found that, just as Mr. Arsem has suggested, there was some oxide there; therefore, we could not measure the occluded hydrogen in that way.

MR. ARSEM: It occurred to me that the presence of oxide might also account for the differences in the rates of corrosion.

PRESIDENT BANCROFT: Isn't it possible to reduce the oxide of iron by hydrogen at a temperature to which these samples are heated occasionally?

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MR. ARSEM: There is not enough hydrogen in the iron to reduce all the oxide. The hydrogen goes off below the reduction temperature; it is all out at 400°.

DR. J. W. RICHARDS: The effect of this small amount of hydrogen amounting to one-fiftieth of one per cent. by weight, is possibly not unknown with other metals. An equal amount of bismuth in metallic gold is known to make the ductile gold so brittle that it cannot be rolled at all. There is also a possible explanation which has not been mentioned, which is: That it is thought that iron exists in possibly three states, Alpha, Beta and Gamma states, and what state this deposited iron is in I don't know that we are prepared to dogmatize upon; whether it is exactly the same state as ordinary iron which has been heated and cooled slowly, or not, we do not know. It may be that the heating changes the iron from this particular state in which it was deposited, to the ordinary state, and some allotropic change like that may account for the difference in corrodibility.

MR. SADTLER: In reading Prof. Burgess' paper I saw that he stated that on heating the electrolytic iron. it corroded less in acid; and I should think that if the hydrogen passes off at low temperatures, we could easily determine whether the improvement was due to the hydrogen or to the fusion of the edges of the crystals, because that would not happen until a much higher temperature is reached.

PROF. BURGESS: My paper has some illustrations which refer to those last two suggestions; and I made reference to it at that time.

PRESIDENT BANCROFT: Speaking of the changes of properties through the presence of small quantities of other metals, we have here some samples of some sodium-lead alloy which Mr. Carrier brought up, which is very soft; and yet, on the other hand, has a distinct ring to it, which, as you know, is not characteristic of pure lead. How much sodium is there in this?

MR. CARRIER: I do not know exactly, but probably less than 2 per cent.

MR. C. A. LITTLE (*communicated*): I should like to ask Messrs. Burgess and Engle if the use of electrolytic iron for generating hydrogen (as proposed at the bottom of page (205) of paper) would not prove more expensive, in the majority of cases, than the direct generation by electrolysis.

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PROF. BURGESS: That depends entirely upon the cost of producing the hydrogen electrolytically and the cost of electrolytic iron. The electrolytic iron at the present time is not available at the price which would enable it to compete with the common methods of generating hydrogen; but, as suggested in the paper, if the demand should be great enough, electrolytic iron could be produced very cheaply, so as to be marketable at a lower price than zinc.

MR. HUGH RODMAN: In generating hydrogen by iron for such commercial uses, as lead burning, or welding, hydrogen is obtained by passing gas from ordinary iron turnings through potassium permanganate. Such hydrogen costs much less than that generated by zinc.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

THE DEVELOPMENT OF THE NICKEL PLATING INDUSTRY.

By Isaac Adams.

Fifty years ago, a little more or a little less is immaterial, the state of the art as regards electro-deposition of metals was about as follows: Copper was deposited from the acid sulphate, with a near approach to theoretical efficiency. Silver and gold were extensively deposited from extremely alkaline solutions with nearly theoretical efficiency. Brass, iron and platinum were also used as covering metals, but only to a trifling extent in comparison with the others. In those days, intelligent workers in the field of electro-chemistry were few and far between. The published works of Smee and Gore in England, Roseleur in France, Elsner in Germany, and a few others whose names I cannot recall, represented all that was known of the practical or industrial art of electro-chemistry. Compared with what there is known to-day, one might say that the art did not exist at all. Notwithstanding the great advances, both in theory and practice, in one respect, however, there has been no change. In the chase after solutions from which metals could be practically deposited, the rule of thumb method prevailed, and had to prevail. Take, as an example, the search for a practical silver-plating solution. Doubtless, hundreds of silver salts were tried before the rather out-of-the-way double cyanide of silver and potassium was found. In the case of untried metals, the experimenter could not safely draw any inferences from similar combinations. There were no rules and few theories to guide. It was a matter of the "cut and try" method of the machinist of that time, and I am afraid it is much the same to-day.

The first commercial nickel plating, so far as I am aware, was carried on in a small room on Fourth street, Boston. The immediate occasion was this: During the years 1858 and 1859, I had been investigating the electrolytic possibilities of many

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nickel and cobalt salts, so that I had become familiar with the properties of these metals, both in the pure, fused condition and in the form of electrotypes. These latter were small sheets of from three thousandths to five thousandths of an inch in thickness, stripped from polished sheets of brass used as cathodes, of about 3 by 4 inches in dimension. Precisely how the thing came about I cannot at this distance of time recollect. It will suffice to say, however, that I somehow managed to interest a Mr. Joseph Smith, of Boston, a dealer in gas fixtures, to start the business of nickel-plating cast-iron gas tips, he to furnish the capital and I to do the plating. So it happened that along in the winter of 1865-66, I commenced operations with about twenty gallons of solution and with cast-nickel anodes. Incidentally, I may say, that I took out a patent at the time (the first nickel-plating patent on record, I believe) for a nickel plated gas tip as a new article of manufacture. First and last I must have plated more than one hundred gross of these iron tips, besides a good many brass ones. The tip was good enough, but, as I learned later, my backer could make more money on the lava tip, which was then beginning to be extensively used, and which, in fact, soon after practically drove all other tips out of the market.

The next attempt to place nickel plated goods upon the market was made in the winter of 1868-69 by Wm. H. Remington, under the firm name, as I recollect it, of Wm. H. Remington & Co.; the company, in this case, being a lady well-known in Spiritualistic circles, and herself claiming to be a medium. Mr. Remington, who had had some experience in electrotyping, represented in the firm the "skilled in the art" man, while the rôle of the lady partner was, in some mysterious way, to control all baneful spirit influences and, if possible, to filch from some unsuspicious spirit, bits of information and knowledge which might be of use to the firm and which could be obtained in no other way. (Whatever has been said or may be said as to spirit influences in nickel plating, is given in part from the writer's personal knowledge, but mostly from testimony given in the case of "United Nickel Co. vs. Anthes," United States Circuit Court Records.)

Mr. Remington had produced in his laboratory samples of nickel plating on articles which could easily be carried about and

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exhibited, such as teaspoons and harness hardware, and these, so far as outward appearances went, were very well done. Early in the winter of 1868-69, Mr. Remington, having previously obtained a backer with the necessary capital, started in to do nickel plating for the public. His principal contribution to the business was a grain-nickel anode, which he patented, the excuse for making and using such an anode being that the metal could not be melted and cast. (Strange as it may appear now, the idea that nickel could not be *commercially* melted and cast was prevalent among both the users and the manufacturers of that day.) Mr. Remington's shop was located in Province street, Boston, Mass., and was well stocked with the solutions and tools necessary to the business. There were several plating tanks holding, in the aggregate, from 400 to 500 gallons of nickel solution, a hot caustic soda bath and a hot cyanide of copper bath. The electrolyte was originally a solution of nickel chloride, with an excess of ammonium chloride; the number of employees was from fifteen to twenty, mostly brass finishers. Mr. Remington used a current of very high voltage, and had to, for lacking that, no nickel was deposited, and if an attempt was made to thicken the deposit, the metal riffled up into minute brownish spangles, a totally useless covering. Twenty-four Groves' cells in series I found attached to one tank. Whether the baneful spirits got in their work here is not known, but Mr. Remington's efforts ended in utter failure. His financial backer, becoming frightened about this time by the continued demands made on him, employed Mr. Moses G. Farmer, an old-time electrician and the father of the fire alarm system, to investigate matters. To make a long story short, I was called in to straighten matters out. Mr. Remington, in the attempt to render his solutions more efficient, used numerous "dopes," mostly of vegetable origin, and with spirit advice. The last "dope" tried was an aqueous infusion of skunk cabbage. The Province street shop was reorganized and called The Boston Nickel Plating Co., and under that name it exists to-day.

About May, 1869, I was advised to take out patents for my process of nickel plating, including the cast anode. This cast anode was certainly "new" and surely "useful," but its validity was never passed upon by the courts. Mr. E. A. Quintard, of

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New York City, Mr. A. Gaiffe, of Paris, France, and a Mr. Sellers, of Sheffield, England, soon after became part owners of the patents. Simultaneously with the restocking of the Boston shop with solutions and anodes, another shop of much larger capacity was planned and opened in New York City. This latter was situated not far from City Hall Square, on Crosby street, I think, but I am not sure of the name. With the facilities we then had for manufacturing nickel anodes and salts, matters went rather slowly; but by the end of July, 1869, both shops were in good running order and with plenty of work. The New York shop was in charge of Mr. Luther L. Smith, a very capable man, who introduced two new things—a department for grinding and finishing brass and steel articles from the rough, and also a Wilde dynamo, the first successful dynamo for plating purposes used in this country. This shop was afterwards known as The New York Nickel Plating Co., and is still in existence.

Late in September, 1869, Mr. Quintard and myself visited England, France and Germany, with the view of establishing the nickel plating industry in Europe. A small experimental shop was located soon after in Liverpool, but by springtime we had a fully equipped plating establishment of about 600 gallons capacity in Birmingham.

A shop under the management of Mr. A. Gaiffe, a well-known manufacturer of scientific instruments in Paris, France, was opened for business in December, 1869. It was located in Paris, in Rue St. André des Arts, and had a capacity similar to the one in Birmingham.

It is almost needless for me to say that we had no competition in the nickel plating business at this time, either in this country or abroad, since outside of our own shops, nickel plating did not exist. The competition, and plenty of it, came later on.

By reason of the fine color and enduring qualities of the covering metal, nickel plating came at once into favor with the public; besides, it was cheap and could readily be used to cover the coarser and heavier articles of commerce, which it served both to beautify and protect. In this country, the industry advanced rapidly, and nickel plating was applied to almost everything under the sun, from watch movements to calender rolls weighing half a ton or more. In England, owing to the ultra

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conservatism of the British manufacturer of that date, the advance was much slower. The Elkingtons, however, at that time the largest silver plating establishment in the world, helped us not a little by placing with us goods to which they thought the "new plating," as they termed it, could be usefully applied. They certainly helped largely to keep the pot boiling in the early stages of our struggle with the British citizen.

In France we had no difficulty whatever. Although nickel plating did not jump into prominence as rapidly as it did in this country, still the Paris shop was on a paying basis practically from the time it was opened for business.

Through the good offices of President Dumas, we were permitted to bring to the notice of the Academy of Sciences samples of electrotypes and plated articles, and, in his presentation speech, he took occasion to compliment the discoverers and to welcome the advent of the "new industry."

This narrative now brings us down to the commencement of the Franco-Prussian War, and I believe that what I have here written covers, historically, all the essential facts relating to the introduction and development of the nickel plating industry. The art is to-day carried on substantially as it was in 1869-70, with the same solutions, the same anodes, and the same details of shop manipulation.

On the following page is given a reproduction of an engraving made more than thirty-five years ago. The engraving is a souvenir of the nickel campaign in France, 1869-1870, and is interesting from the fact that it was struck off from a nickel electrotype (clichè), undoubtedly the first of its kind. The print purports to be the portrait—taken from a distance—of the oldest child of Louis XVI. and Marie Antoinette during their confinement in the "Temple." The original was an engraved copper plate which my friend Gaiffe found among his collection of bric-a-brac.

We know that after a certain number of impressions have been struck off from an engraved metal plate, it begins—to the expert at least—to show signs of wear or "fatigue." It occurred to M. Gaiffe, from what he observed as to the hardness and toughness of the deposited metal, that a nickel electrotype made from an original copper plate might equal and perhaps surpass in endurance an engraved steel plate, while preserving the original

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Madame Royale

Au Temple en 1793

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intact. He accordingly enlisted with him in the trial, a printer of his acquaintance. Some fifteen hundred impressions were taken, and it was quite impossible to distinguish between the earlier ones and the later ones.

Cambridge, February, 1906.

DISCUSSION.

PRESIDENT BANCROFT: Mr. Adams says that a rolled anode was introduced by Mr. Wharton, but that this rolled anode did not prove a success. It seems to me, speaking as a layman, that there is very great opportunity for improving the art of nickel-plating. The electrolyte which is ordinarily used is ammonium nickel sulphate solution. In that solution, pure nickel as anode is practically passive, and, consequently, there is no corrosion. To get around that, the cast anodes contain iron; I am told, from 6 to 10 per cent. of iron. One sample that we bought in the open market and analyzed, contained a trifle over 6 per cent. of iron. Under those circumstances, the nickel anode does not become passive so readily in sulphate solution; and the difficulty has been eliminated to a certain extent. To my mind, however, we have introduced a great many more difficulties than we have eliminated. The iron dissolves with the nickel as ferrous sulphate; a certain portion of it is oxidized by the air and goes over into ferric sulphate, is hydrolyzed, and precipitates as ferric hydroxide; but I am certain, from experiments that we have made, that some of the iron remains in solution as ferrous sulphate. From a solution containing ferrous sulphate and nickel sulphate, at least the same percentage of iron is precipitated as occurs in the solution; consequently, the conclusion that I draw (and I hope we may get some information from people that know more about it than I do) is, that all our nickel-plate contains iron. I am confirmed in that belief by the fact that the nickel-plating on the Weston instruments, which I assume to be as good nickel-plating as any that would be put on the market, rusts red in the laboratory. I take it that this is due to iron in the nickel-plate. Of course, there is nothing gained by pitching into the use of cast anodes containing iron, if

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one has not any suggestion as to getting around the difficulty. You can take a pure nickel anode and you can stick to your ammonium nickel sulphate solution, if you want to. If you will add a slight percentage of ammonium chloride or nickel chloride, the pure nickel anode will dissolve with nearly a hundred per cent. efficiency. If there is no iron in the anodes, you introduce no iron into the solution, and, consequently, you introduce no iron into your nickel-plate. It seems to me that this is the way that nickel-plating will be done in the future. If we do that, we shall get nickel-plate which will stand.

I have already referred to the case of the nickel on the Weston instruments. If a bicycle is left out over night, it will rust. It seems to me that that particular difficulty was encountered, and that it was avoided in a way which is, so far as I can see, a very poor one. We know a thoroughly satisfactory way of getting around the difficulty of a passive anode, and there is no obvious reason, from a University standpoint, why we should not have nickel-plating which shall consist of nickel, not of iron. Perhaps some one can supply the information (which I have not got) which would account for the continued use of what is causing an unsatisfactory state of things so far as my information goes.

MR. CARL HERING: If the function of the iron in those anodes is to help dissolve the nickel by local action, why not fasten a little plate of platinum or carbon to the anode instead, so as to produce that local electrolytic corrosion without contaminating the liquid?

PRESIDENT BANCROFT: I did not say that the object of the iron was to make the nickel dissolve by local action. I said that an iron-nickel alloy corrodes; that under those circumstances, nickel does not become passive. It is not a case of local action; and as a matter of fact, you can show that if you put your piece of platinum in contact with the nickel, the nickel does not dissolve. It is the reverse case of the one that we have had in the bronzes. In the latter case, we have had certain alloys of copper or tin which corroded much less readily than either copper and tin; in the case of the iron-nickel alloys, we have an alloy which corrodes less readily than iron, but much more readily than pure nickel. It is not in any sense a question of local action.

PROF. C. F. BURGESS: The reason that is usually given for the

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use of the double sulphate is, that it produces a harder and more durable deposit, mechanically speaking. My observation seems to bear out this conclusion. I deposited layers of nickel from the chloride solution, and found that the deposit is much softer than can be obtained from the double sulphate bath ordinarily used.

PRESIDENT BANCROFT: You notice that I have not suggested changing over to chloride solution, but merely the addition of a small amount of chloride. This leaves the solution essentially a sulphate solution, and I believe will not change the quality of the deposit at all. It seems to me you can have all the alleged advantages of the sulphate electrolyte at the cathode, with all the known advantages of the chloride at the anode. It is not often that you get things both coming and going; but I think you do there.

MR. CARL HERING: I am sorry that somebody who is more familiar with nickel-plating does not reply to the statement in the paper that we have made absolutely no progress since 1870. It will appear in the records of our transactions as apparently true, because nobody in this society has replied to it. It seems to me it is very strange if we have not made any progress at all in thirty-six years.

(Communicated after Adjournment.)

MR. N. S. KEITH: In what I have to say, I wish to be understood that I do not intend to belittle what Dr. Adams and his co-laborers, the United Nickel Company and its licensees, did in the '70s toward establishing the nickel-plating industry. What was done was done under the stimulus of the patents granted to Remington and to Adams separately; Remington's being of an earlier date.

No matter what may now be said about the Remington methods, the fact remains that his patent was deemed of enough value to warrant its purchase by the organizers of the United Nickel Company, which also purchased the Adams' patent (hence

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the title "United") incident to the endeavor to monopolize electroplating with nickel.

There is no question in the minds of those acquainted with the facts, that Remington with his chloride solution, did some very good plating, and also some very bad. The same conditions existed for a long time with those who used the double sulphate solutions. And these results prevailed until, as the result of experience, the operators had learned the requisites for success, such as a thorough polishing of the surfaces to be plated, and their absolute cleanliness before immersion in the bath. More failures came from neglect of these precautions than from any other one reason. Next to these came the proper care for the proper anodes, especially the extent of their surfaces compared with the average extent of surfaces of the cathodes; so that, on the one hand, more nickel was not deposited than entered the solution from the anode, or, on the other hand, too much nickel was not dissolved. In either case the integrity of the solution was impaired and imperfect work was the result.

It is not necessary at this late day to discuss these vital points which are now so much better understood, but I may not forbear to call the attention of the Society to the unique patent to Dr. Adams of 1869. It was under this patent that the United Nickel Company sued right and left, alleging infringements.

The main claim of the patent was in words as follows: "In nickel plating the use of a solution of double sulphate of nickel and ammonia made so as to be free from potash, soda, lime, alumina and nitric acid, or any acid or alkaline reaction."

How a solution of double sulphate of nickel and ammonia could exist with soda, or lime, or alumina, *as such,* in it, is a riddle. Nitric acid seems to be altogether extraneous, unless it might be thought a possible introduction could come from careless use of the "dips" of the plater. The absence of either acid or alkaline reaction is to be taken for granted with the salt of double sulphate of nickel and ammonium. Simmered down, this claim is for the use of a *pure* solution of the double sulphate.

In justice to the U. S. Patent Office, I may say that it was granted when applications in chemistry, electrometallurgy, metallurgy, physics, electricity, and other branches were passed upon by *one* examiner, Prof. Hedrick, a very genial man who believed

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in the British plan of giving about every applicant a patent, and "let him fight it out in the Courts."

I was one of the alleged "infringers." Having found out by experiment, that tartrates so controlled the solution, that a wider margin either side of neutrality of the double sulphate solution might be used and get good results, I patented the new combination and entered the industry, using Rochelle salts as an addition to the double sulphate. I felt safe because I had introduced both potash and soda, though, of course, as a salt of those alkalies, the only state in which they could exist in the plating solution.

I was sued as an infringer. To make a long story short, the decision was against me. The learned judge said that though both potash and soda were in my solution, yet, substantially and in effect they were absent, because as tartrates, their deleterious effects were neutralized, and therefore they were *non est.*

But give to Dr. Adams the credit of establishing the nickel plating industry, for he was its foster father, in that he and his licensees reduced the imperfect science to a practiced art.

(Communicated after Adjournment.)

DR. ADAMS: Notwithstanding the lapse of thirty-four years (time enough, one would think, to make up one's mind,) Dr. Keith appears still to have a confused idea as to what happened to him in 1872.

The Adams nickel patents of 1866 and 1869 (the only nickel patents ever in litigation) were in the lime light almost from the time they were issued until the end of their respective terms. Their scope and validity are matters of court record, are in the nature of *res adjudicata,* and I cannot conceive of any conditions under which a discussion of their merits or demerits would interest the members of this Society. Dr. Keith's plea in defence of Dr. Hedrick and the patent office, in substance asking the members of the Society to condone their faults, faults due solely to a combination of good nature and ignorance, is ingenuous, not to say generous.

Between the years 1871 and 1886 there were tried before cir-

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cuit judges of the U. S. Courts in Massachusetts and New York five separate cases, on final hearing, with full printed records and able counsel on both sides. In each and every case the patent (1869) was sustained and decrees allowed.

I do not propose to be behindhand in generosity, and so I have to ask the members to extend Dr. Keith's apology in such manner as to include these amiable but untutored judges who were in the same boat with Dr. Hedrick and the patent office officials.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

ELECTROLYTIC PRECIPITATION OF LEAD FROM ACETATE SOLUTIONS.

BY RALPH C. SNOWDON.

Under ordinary conditions the electrolysis of lead acetate solutions gives large feathery crystals of lead which fall from the cathode to the bottom of the cell. Even if an excess of acetic acid be added, there is no marked change in the size of the crystals or in the quality of the deposit. This solution seemed, therefore, an admirable one on which to try the methods which had previously proved successful with silver nitrate.[1] It had been shown that rapid motion of the electrolyte, produced either by rotating the cathode or by stirring, tends to make the deposit smoother and to reduce the size of the crystals. It was also shown that the size of the crystals of deposited metal decreases with increasing current density at the cathode until conditions are reached where the speed of the rotating cathode is not sufficient to burnish the rapidly precipitated masses of metal.

Following out the "chemistry" conception of electrolytic precipitation I used a solution of lead acetate and acid, normal with respect to each. Knowing from much previous experience that a satisfactory deposit of lead could not be obtained without stirring, I tried a rotating cathode made of a copper tube having a wetted surface of 10 cm^2. This was speeded to about 2,500 revolutions per minute. A lead anode was used. At a low current density, 0.5 amp/dm^2, the metal deposited from this solution in a crystalline and adherent form, almost entirely without the "flaky" appearance which is so noticeable with a stationary cathode. At higher current densities, however, the deposit kept growing worse and worse, falling off in leafy crystals. This was probably because the speed of rotation of the cathode was not high enough

[1] Snowdon, Jour. Phys. Chem., 9, 392 (1905); also Trans. Am. Electrochem. Soc., 7, 143 (1905).

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for the speed of precipitation, the two always being interdependent to a greater or lesser extent.

Since it was not feasible to increase the speed of rotation of the cathode, I next tried the addition of gelatine to the solution. One gram of gelatine per liter was added; the temperature was kept at 30°; the cathode density was 1.5 amp/dm²; and the other conditions were as in the preceding runs. A matted deposit of lead was obtained, very adherent and entirely satisfactory in every way. It is not claimed that a lead acetate solution would be a desirable one to use in precipitating lead. There are other solutions, notably the fluosilicate, which give an adherent deposit of lead over a much wider range of conditions. The object of the paper was to show that it is quite possible to get a good plating deposit of lead even from an acetate solution, and that the favorable conditions are the same for lead as for other metals.

This work was suggested by Prof. Bancroft and carried out under his direction.

Cornell University.

DISCUSSION.

MR. CARL HERING: It does not appear quite clear whether or not there was rotation when gelatin was used. The author says, the conditions are the same as in the preceding runs; but in some of those there was rotation, and in others there was not.

MR. SNOWDEN: I said in the second paragraph on page 1, "Knowing from much previous experience that a satisfactory deposit of lead could not be obtained without stirring, I tried a rotating cathode;" and that rotating cathode runs right straight through. This run on the first page was with the rotating cathode; and the one on the second page was made in the same way. I have said "the temperature was kept at 30 degrees; the cathode density was 1.5 amp-dm²; and the other conditions were as in the preceding runs."

MR. HERING: Then I understand that without this rapid motion such a deposit could not be obtained; that is, the rapid motion is absolutely necessary to obtain this deposit.

PRESIDENT BANCROFT: So far as our experience goes.

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DR. C. S. PALMER: This was at the cathode, was it?

PRESIDENT BANCROFT: Yes.

MR. S. S. SADTLER: Reference has been made at different times to the use of gelatin and gum arabic and the statements made as to their being reducing agents and colloids. Gelatin does not dissolve in water but is swollen the same way as gum arabic. There are several of those gum substances which are not truly dissolved in water. I was wondering if maybe the physical property of such finely suspended substances would have some special influence on the deposits from this fact rather than that they were colloids in the sense that they were not crystalloids.

PRESIDENT BANCROFT: That property rather comes in under the statement made of its being a colloid. Personally I don't care to classify gelatine as a reducing agent. I would rather class it as a colloidal substance.

MR. SADTLER: A colloid is a non-crystalloid.

PRESIDENT BANCROFT: No, we have got a later definition than that, I think. You will find a distinction between solutions and colloidal suspensions in the paper by Mr. Whitney, read at Boston last year.

MR. HERING: What is the new definition of a colloid?

PRESIDENT BANCROFT: I referred to Mr. Whitney's paper because I was not able to give the definition off-hand.[1] As you were present and heard that paper read, doubtless you can tell us.

DR. J. W. RICHARDS: I wish I could—I have wished many a time that I could say in some definite words to my students what the effect of adding these colloids to the solution was; that is, the rationale of this effect; but it certainly is not due to the reducing action. It appears to me that it is the effect of the added substance upon the crystallization of the deposit; that is, upon the adhesion of one crystal to another and the growing out of the crystals in one direction. It apparently breaks up the tendency to the crystals' attaching themselves one to another, as they do ordinarily in a lead deposit from nitrate solution.

PRESIDENT BANCROFT: I doubt very much whether the deposit is pure metal in any case where we have a colloid in solution. We know that in the straight chemical precipitation of colloidal

[1] Amer. Electrochem. Soc., 7, 225 (1905).

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metals the metal is never pure. We know that the addition of carbon bisulphide for silver-plating solution gives you bright silver and that that silver is not pure. My belief is that in all these cases we should probably find on analysis that the metal was not pure, and that that was the reason why it did not come down in so markedly crystalline a form. That is a side of the matter which for the time being has not seemed quite so important; and consequently we have made no careful analysis; but we know from experiments made at the University of Pennsylvania on electrolytic precipitation of metals from solutions of so-called organic acids, that there is always great danger of a certain amount of carbon coming down with the metal; so that there is certainly a very great plausibility for the belief that the metal is never absolutely pure under those circumstances.[2]

MR. E. A. SPERRY: I thought that, to the contrary, very careful analysis had been made of metals so deposited and on a very large scale by Mr. Betts; and those certainly show a very high degree of purity indeed, as is evidenced by the analyses themselves which we have in our records; and, besides that, Mr. Betts has stated, I think, in one of our meetings, that there is an attendant increase of voltage when gelatin is present that may help to explain to some extent the nature of the deposit; I mean that the voltage is always slightly increased when the gelatin is present, although in an extremely minute proportion. It seems to me that that is a definite result and is probably producing in some way the changed form of deposit.

PRESIDENT BANCROFT: I did not remember that Mr. Betts had made any careful analysis which would show the presence of one part in one thousand or thereabouts of carbon in his electrolytic lead. If he has, I should have to modify my statement.

MR. SPERRY: I could not say as to the exact analysis for carbon; but analyses have been shown, as I remember, that go down to the fourth place per cent., which are millionths, with the result that the lead is of extreme purity.

MR. H. E. PATTEN: I hardly see that Mr. Sperry's point bears upon the question of the influence of the colloid in bringing down an impure coating, for this reason; that we know that the floccu-

[2] Since the meeting, a paper by Müller and Bahntje has been received, which throws light on this subject. Zeit. Elektrochemie, *12*, 317 (1906).

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lation of colloids can be induced by very minute quantities of material and the amount of material that is required to change the state of a vast amount of colloidal solution is very, very small. I happen to have read Mr. Betts' paper with considerable interest recently, because just at present I am working upon some surface action phenomena and colloidal solutions in general; and my remembrance of Mr. Betts' own statement in regard to that was, that he could not positively say that this effect was due to the substance because it was a colloid, but he had gotten similar effects from other substances which were not colloids. He seemed to think that it was the action of a minute quantity of added substance which changed the nature of the deposit. A colloidal solution so-called, or suspension, such as ferric hydroxychloride shows a great many of the properties that finely divided particles such as quartz, platinum and gold do; so that this change in the nature of the metallic deposit is apparently due to a surface action, which splits the salts preparatory to the final deposition.

MR. G. A. HULETT: Silver deposited from the acetate solution is very compact and shows no suggestion of a crystalline surface. Some very exact work has been done on this in connection with the silver voltameter by Lord Rayleigh, who found that this compact non-crystalline deposit from the acetate solution was distinctly heavier than the crystalline deposit from the silver nitrate solution. The two voltameters were in series.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

STRUCTURE OF ELECTRO-DEPOSITS.

BY CHARLES F. BURGESS AND OLIVER P. WATTS.

It is a well-known fact that electro-deposits may be made to exhibit a great variety of physical structures; in fact, it has been suggested that all forms of vegetation may be imitated in metal, deposited electrolytically. It is not the reproduction of the various forms of vegetation, but rather the prevention of their formation that measures the success of deposition for technical purposes.

The factors which influence the structure are, current density, temperature, circulation of solution, composition of electrolyte, gases, or other impurities dissolved in the electrolyte, and the thickness of the deposit.

It is not the purpose of this paper to discuss in detail the influence produced by a variation of each of these factors, but rather to point out some peculiarities of the physical structure of electrolytic iron. These observations are incidental to an investigation of the production and properties of electrolytic iron now in progress under a grant from the Carnegie Institution of Washington.

With suitable adjustment of the factors above named, it has been found that the deposition of iron in thick layers may be carried on with almost the same ease and rapidity as is the case with copper and some other metals.

One of the difficulties which may be encountered in the deposition of iron or other similar metals is vertical grooving, as illustrated in Fig. 1. This appears to be due to the upward flow of the electrolyte at the cathode surface, the dilute solution flowing upward through channels which conform to and start from protuberances near the bottom of the cathode. Among the methods of preventing this grooving are agitation of the solution and the proper choice of solution density and composition. The addition of an inert salt will diminish the changes of specific

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gravity of the electrolyte in the neighborhood of the cathode, due to depletion of electrolyte by deposition of the metal.

Another troublesome feature is that caused by gas bubbles adhering to the deposited metal. These bubbles insulate the portions of the plate beneath them, thus producing pitting, and the metal may even pile up around the bubbles so completely as entirely to enclose them. Fig. 2 illustrates a surface in which the influence of gas bubbles is apparent, the light portions representing the ridges between bubbles. It is commonly assumed that these gas bubbles are due to the liberation of hydrogen, but it is the belief of the authors that air may be equally

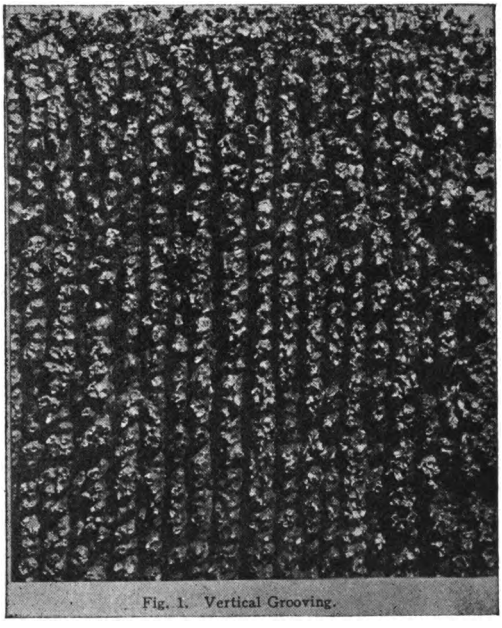

Fig. 1. Vertical Grooving.

responsible with, or more so than, hydrogen in giving rise to this trouble. In the deposition of iron, it has been found that the gas pitting is more pronounced with a solution freshly prepared than it is after the current has been flowing for some time. Also that after allowing the solution to stand idle for some time, the gas bubbles will be copiously liberated when the cell is again started. Agitation of the electrolyte by blowing air through it, is not practicable, through the increased liberation of the gas

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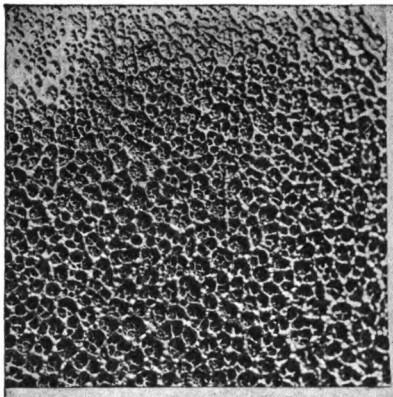

Fig. 2. Pitting Produced by Gas Bubbles.

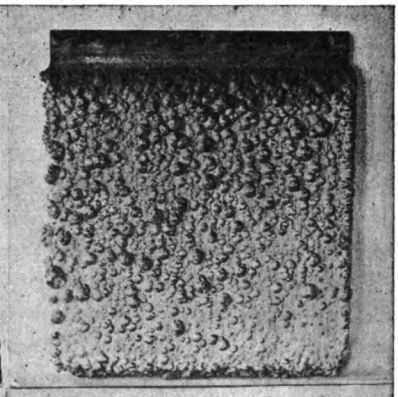

Fig. 3. Iron Cathode, two months growth.

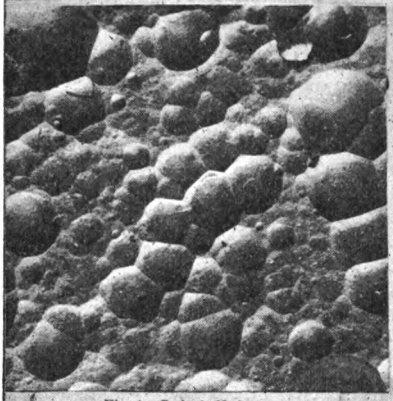

Fig. 4. Cathode Nodules.

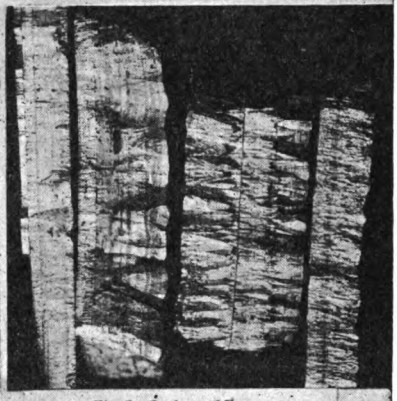

Fig. 5. Surfaces of Fracture.

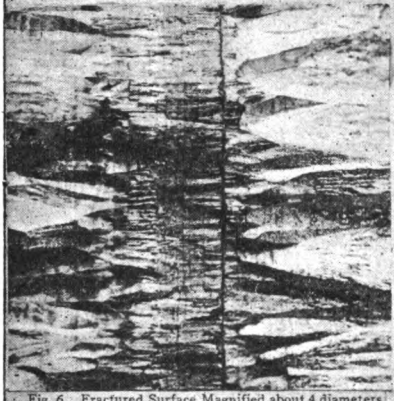

Fig. 6. Fractured Surface Magnified about 4 diameters showing starting sheet.

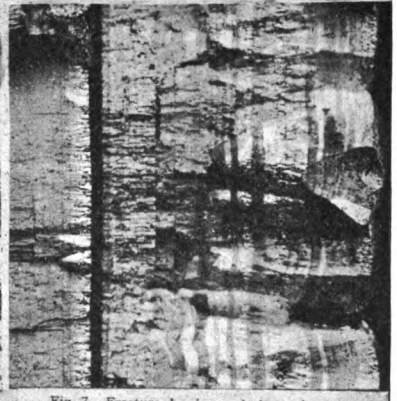

Fig. 7. Fracture showing conical growths.

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caused by it; and, in fact, the deposition proceeds most satisfactorily if air is kept, as far as possible, away from the solution. It is well known that air is soluble to a certain extent in various solutions, and it appears that the flow of the electric current has the effect of driving this air out of the electrolyte onto the cathode. A remedy which may be used for overcoming this defect, at least in the case of iron, is to boil the solution, driving out the air as far as possible.

Employing a current density of about ten amperes per square foot, temperatures between 20° and 30° C., a solution of ferrous sulphate and ammonium chloride, with a centrifugal pump for circulating the electrolyte through the series of tanks, and, observing precautions for the exclusion of dissolved gases, it has been found possible to deposit iron to a thickness of at least 1 inch. The thickness is usually limited by the degree of roughness on the surface. The iron made during the first few days of deposition appears smooth; later, small irregularities may become apparent, and these increase in number and size as the process is continued.

Fig. 3 illustrates a cathode of iron in which the deposition has proceeded for two months.

Fig. 4 illustrates more in detail the appearance of the surfaces, showing nodules in various stages of development. The convex hummocks vary in size from those which require a microscope to detect them to those which measure ½ inch or more across. The natural form of these growths is of a circular cross section, the diameter increasing steadily with the thickness of deposit. Where two of these growths interfere, deformation takes place, producing a honey-comb appearance, as shown in the group near Fig. 4.

Just what produces these characteristic growths is perhaps, a matter of speculation. The ideal deposit is one which is dense, homogeneous, and smooth on the surface. It is possible that the roughness of the iron deposit just referred to, may be due to minute particles of impurity suspended in the electrolyte, which attach themselves to the surface receiving the deposit. The current tends to cover up such particles, and the hump thereby produced, steadily increases in magnitude. This is commonly offered as the explanation, though we have been unable to find such particles with a microscope.

Fig. 5 illustrates the fracture of four different iron cathodes,

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the lower one being a dense and rather smooth deposit and the one above showing how such dense deposit may assume that peculiar structure which makes itself apparent on the surface in Fig. 4. The third section in Fig. 5 shows a deposit in which the cones grow in both directions from the starting sheet. The difference in thickness on the two sides of the starting sheet, is due to the variation in the current density on the respective sides. The top section shows an electrolytic deposit which is of a fibrous nature.

Fig. 6 shows a larger magnification of the fracture, and the growths which appear to take root near the surface of the starting sheet and extend onward, are quite apparent.

Fig. 7 shows two fractured cathodes, the larger illustrating the characteristic tooth-like growth, and the other demonstrating that by acidifying the solution, the conical growths may be suppressed until the plate has attained a considerable thickness. If the nodular deposits are struck a sharp blow with a hammer, some of the conical-shaped growths will become separated from the main body of the metal, leaving cavities sometimes ½ inch or more in depth. A group of these teeth which were collected in breaking up an iron cathode is illustrated in Fig. 8. It will be noted that some of them are almost perfect cones, while the sides of others show interferences produced by adjacent growths.

Another characteristic which is prominent in most of the figures referred to, is shown by the lines parallel to the starting sheet, which indicate surfaces of cleavage along which the metal is liable to separate when mechanically disintegrated. These surfaces of cleavage seem to be produced when any marked change in or interruption of the depositing process occurs. If the current is interrupted for a time, or if the cathodes are removed from the tank and exposed to the air, a cleavage surface may be produced. It is also believed that a sudden change in the current density may have the same effect. The differences in structure produced by variations in the current density are illustrated in Fig. 9, which is a fracture at right angles to the surface of deposition, which had been polished, etched, and magnified to seventy-one diams. The strata which are shown and which average 2 mm. in thickness, indicate the thickness of iron deposited each day of twenty-four hours. Striations are the

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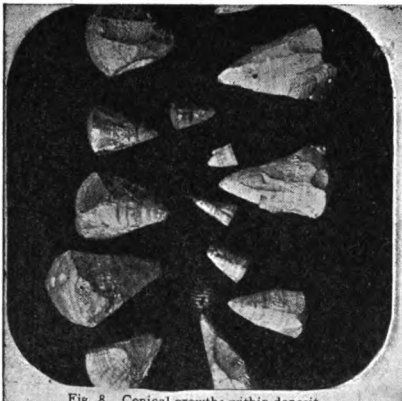

Fig. 8. Conical growths within deposit.

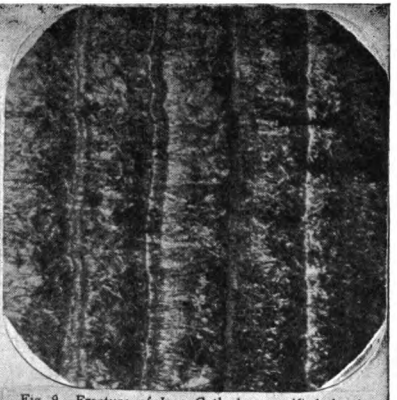

Fig. 9. Fracture of Iron Cathode, magnified showing layers deposited each day.

Fig. 10. Polished Section of Nodule.

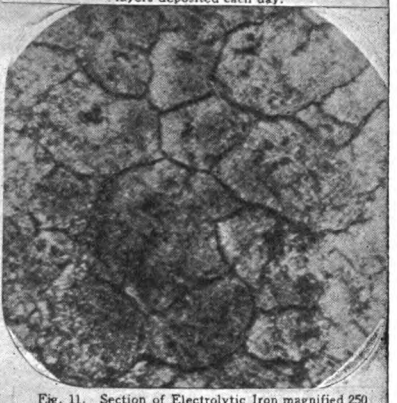

Fig. 11. Section of Electrolytic Iron magnified 250 diameters.

Fig. 12. Electrolytic Iron heated.

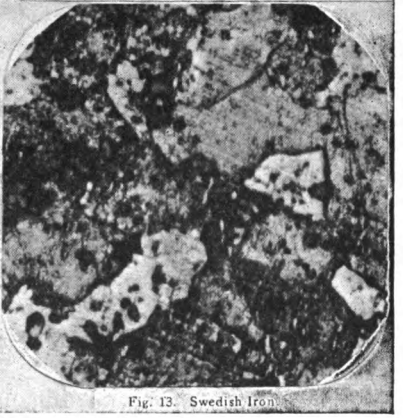

Fig. 13. Swedish Iron.

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result of varying the current density, due to the method of operating the plant, which consisted in charging storage batteries in series with the iron cells for eight hours, and discharging at a lower current density for the remainder of the twenty-four hours.

Fig. 10 shows a polished and etched section of one of the nodules, such as are illustrated in Fig. 8. This reveals the laminated structure of the nodule, the magnification being twenty diams. and not sufficient to show the granular elements of the mass, as in Fig. 11, which is a magnification of the previous section to 225 diams. This reveals the fact that the mass of the iron is made up of grains bearing a striking similarity to ferrite, but differing from the normal ferrite structure in the absence of visible orientation of crystals composing the grains. The characteristic ferrite structure may be developed, however, by heating electrolytic iron; Fig. 12 shows such structure produced by heating electrolytic iron to about 1,000° C., polishing and etching the section, and magnifying to 132 diams. The light and dark patches are due to the different orientation of the crystals which go to make up the separate grains of ferrite. The unrefined iron, when subjected to the same treatment and magnification, is illustrated in Fig. 13, in which we have the typical ferrite grains. The black spots distributed throughout and between these grains are attributed to slag fibres which are contained in the Swedish iron, and which are entirely absent from the electrolytic iron.

That the characteristic nodular structure of electrolytic deposits is not peculiarly an electrolytic phenomenon is shown by the striking similarity of these deposits to those which are produced in nature. Figures 14 and 15 show two surface photographs taken from electrolytic iron and hematite. Fig. 16 is a similar photograph of the surface of a mass of manganite. Several other minerals that have resulted from deposition from a solution show a similar appearance.

This striking similarity of structure between certain minerals deposited by natural processes and some of the products of electrolytic deposition are not confined to the surface, but extend throughout the materials, as is seen in Figures 17, 18, and 19, which are photographs of fractured specimens of hematite, of limonite, and of electrolytic iron, respectively.

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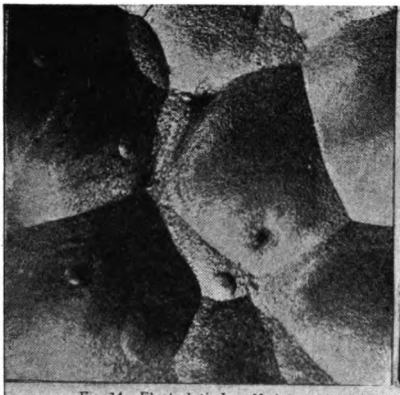

Fig. 14. Electrolytic Iron Nodules.

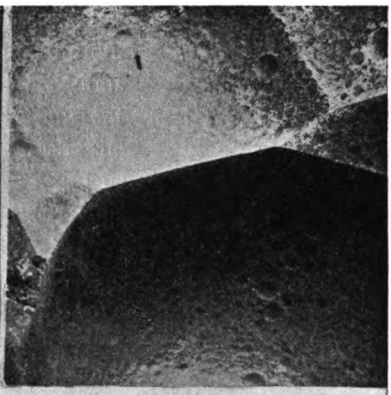

Fig. 15. Hematite.

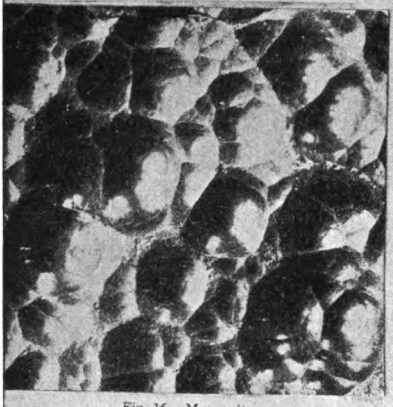

Fig. 16. Manganite.

Fig. 17. Fracture of Hematite.

Fig. 18. Fracture of Limonite.

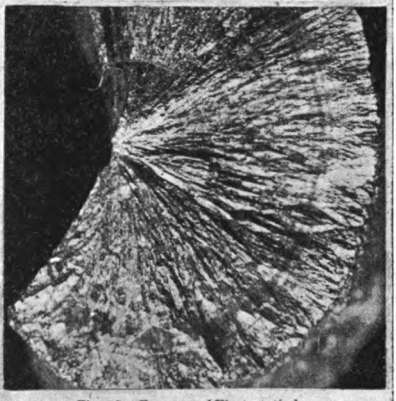

Fig. 19. Fracture of Electrotytic Iron.

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Manganite has a similar fracture. In view of these facts, the time may yet come when the geologist, seeking better understanding of the natural deposition of minerals from solution, will experiment in the laboratory, and with the aid of the electric current, be able to observe during their growth and obtain, in a few weeks, forms which in nature required years for their production. It is well, too, that the electrochemist should keep in mind that the process of deposition, as carried out by means of the electric current in the laboratory, although an artificial process, is yet closely related to such examples of natural depositing as have already been cited, and, in so far as the two processes are alike, must be subject to the same laws.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

MR. S. S. SADTLER: I would like to ask what differences in the structure are noticed by increasing the rapidity of deposition of the iron,—whether you succeeded in getting much smoother deposits.

PROF. C. F. BURGESS: That was one of the problems we had to meet—to find the current density that would give us the best deposit; and we found that that range was rather small, lying between 5 and 15 amperes per square foot. Of course, the current density had to be adjusted in conjunction with the other variable factors; and the influence on the physical structure which a change in the current density would make, depends upon what your adjustments of temperature, circulation and other factors are. It is hard to state what the effect of current density is on the physical structure.

MR. SADTLER: The range is not quite as great as in copper or silver depositing, is it?

PROF. BURGESS: Well, I think it is. The trouble comes in getting thick plates. We can use a great range of current density for iron if we want to get only a film of it; but when we come to get thick plates the trouble develops.

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PRESIDENT BANCROFT: Is your commercial scale so colossal that you could not afford to stir your solutions vigorously?

PROF. BURGESS: We stir by circulating it. By putting a stirrer in each tank we would agitate the solution so much that it breaks up the film that forms on the surface, thereby letting in too much air.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, held at Ithaca, N. Y., May 2, 1906, President Bancroft in the Chair.

THE CADMIUM STANDARD CELL.

By George A. Hulett.

The combination proposed by Edward Weston: Cd — amalgam $||CdSo_4 8/3H_2O\ Hg_2SO_4||$Mercury; has so much lower temperature coefficient than the Clark cell that a very considerable amount of work has been done on testing its reproducibility and constancy. Observations on a large number of these cells have been published by Jaeger and St. Lindeck,[1] and indicated a reproducibility of one part in 10,000. They concluded that the cell was an eminently suitable standard of E. M. F., and that the outstanding variations were due to variations in the mercurous sulphate used as depolarizer.

In 1903, the electrolytic method of preparing mercurous sulphate from dilute sulphuric acid and mercury was devised by the author and independently by Dr. F. A. Wolff, of the Bureau of Standards. The first cells made with this electrolytic mercurous sulphate as depolarizer were the 4(D) cells of Dec. 21, 1903, and the 10(F) cells of Feb. 15, 1904. These cells agreed among themselves to one part in 100,000, assumed their constant value at once, but were .00028 v. lower than cells made in the old way with commercial mercurous sulphate.

These cells seemed so much superior to those made according to the old specifications, that attention was at once turned to thoroughly testing the preparations of mercurous sulphate made by the electrolytic method, with the result that one may use any strength of sulphuric acid, from concentrated to molecular, in preparing the sulphate. But with a less than molecular acid, the product formed, gave a high and variable value to the E. M. F. of the cells in which it was used as depolarizer. The current density used in preparing the electrolytic mercurous sulphate may be as great as 5 amperes per 100 cm^2 mercury anode surface,

[1] Zeit. Instk., *21*, 33 (1901).

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and with the higher current densities the product is gray, due to finely divided mercury, is more uniform in size of particles, and gives the best results in cells. For the details of the method of preparation.[2] Here it was also shown that the electrolytic preparation is sufficiently coarse grained to avoid the effect of the size of the particles on the solubility. This might affect the E. M. F. of the cell, as has been pointed out by H. V. Steinwehr,[3] and is an objection to the exceedingly fine-grained commercial preparations.

After these details had been worked out, and the (D) and (F) cells had been under observation for two years, six (A) cells were made. The materials and construction were, as nearly as it was possible to make them, a duplication of the (D) and (F) cells, but these new cells *were .00011 v. higher than the older ones.* More cells were made with different samples of electrolytic mercurous sulphate and with variations in the other materials and in the construction, but they all agreed with the new (A) cells.

Fortunately, ten Clark cells were made on March 15, 1904, and with some of the same electrolytic mercurous sulphate which had served as depolarizer in the (F) cells. These Clarks did not show the usual "ageing," but appeared to be constant from the first. After two years, however, they appear to have slightly increased in value (.00011 v.). The cadmium cells had been assumed to be constant and had been made the basis of comparison. If the Clarks had been assumed constant and made the basis of comparison, the cadmium cells would, of course, appear to have decreased by this .00011 v., and the difference between the and old cadmium cells could then be explained by a slow change in the cadmium cell. More Clarks (cells H11 to H16) were made July 30, 1905, and electrolytic mercurous sulphate was used for the depolarizer. Also, on February 25, 1906, the Clarks (H17 to H21) were made, and for depolarizer, some of the same sample of electrolytic mercurous sulphate was used as was employed for the new (A) cells. The following table gives some of the many observations that have been made on these cells. The values given have been recalculated from the comparisons, on the assumption that the Clarks have main-

[2] Hulett, Phys. Rev., *22*, 338 (1906).
[3] Zeit. Instk., *25*, 206 (1905).

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tained a constant value. The comparisons of March 18, 1904, March 24, 1905, and August, 1905, were made at 18° and 21.1°, but calculated to 25° for the sake of comparison with the later and more important observations. (These cells follow the accepted temperature coefficient very exactly, and the calculated values are entirely reliable.)

Cell	Date	Mar. 18, '04	Mar. 24, '05	Aug. 15, '05	Dec. 14, '05	Mar. 4, '06
D4	Dec. 21, '03	1.01842	1.01831	1.01828	1.01832	1.01832
F1	Feb. 15, '04	42	31	27	30	32
F2	" "	42	32	26	31	30
F3	" "	42	32	28	32	31
F4	" "	42	31	28	32	32
F5	" "	42	32	32	31	33
F6	" "	42	32	27	32	33
F7	" "	42	32	28	34	32
A1	Oct. 21, '05				1.01843	1.01843
A2	" "				43	43
A2	" "				43	43
A3	" "				43	43
A4	" "				43	43
A5	" "				43	43
A6	" "				43	43
H2	Mar. 15, '04	1.42040	1.42040	1.42038	1.42038	1.42040
H3	" "	40	37	38	—	40
H4	" "	40	38	37	40	43
H6	" "	39	—	42	37	40
H7	" "	41	41	44	38	40
H8	" "	41	40	41	—	40
H11	July 30, '05				1.42040	1.42041
H15	" "				41	41
H16	" "				41	41
H17	Feb. 25, '06					1.42039
H18	" "					39
H19	" "					40
H20	" "					38
H21	" "					43

The cells are all maintained in a large oil bath which is electrically heated and controlled. The temperature remains constantly at 25° C. to within 1/50°, and the comparisons are made with a Feussner potentiometer and sensitive D'Arsonval

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galvanometer, which gives 2 mm. on the scale for .00001 v. The values here given are based on the determination of the value of standard cells in absolute units just made by Dr. Guthe.[4] The determination was made on some of the cells I now have, and the value of these Clark cells, made with electrolytic mercurous sulphate as depolarizer, at 25° (the temperature of the measurement), is 1.42040; this gives a calculated value of 1.43300 volts at 15°, and is the basis to be used in the future work. (Clark cells made according to the old specifications and with commercial mercurous sulphate, are, after ageing, .00030 v. higher than these Clarks with the electrolytic.)

It is to be observed that the new cadmium cells (A1 to A6) are now .00011 v. higher than the old (F) series, and that the values of the new (A) cells are very close to the values that the (F) cells originally had. This observed change in the E. M. F. of the cadmium cells is not a peculiarity of the electrolytic mercurous sulphate, as some cells were made in the old way with commercial mercurous sulphate, in November, 1903, and again in November, 1905, a cell was similarly constructed. These cells had the usual high value at first, and settled down to an apparently constant value in about a month, but the old cells are now .00010 v. lower than the new.

It is especially to be noted that the Clark cells, made on three different dates and with different samples of electrolytic mercurous sulphate as depolarizers, are now all in good agreement. Also the depolarizer of the older Clarks was from the same sample as served for the (F) cadmium cells while the same sample of mercurous sulphate was used for the new (A) cadmium cells and the new Clarks (H17 to H21). These facts, with their present values seems to be good evidence that the cadmium cell is not a system in equilibrium, while the Clark appears to be entirely constant.

In the literature there is some evidence of this same thing. F. E. Smith[5] records observations on six cadmium cells made in April, 1902, and one cell made in June, 1904, all from exactly the same materials. The older cells are now .00007 v. lower than the new one. This observed change in the E. M. F. of the cadmium cell is small and slow, and from the practical standpoint,

[4] Phys. Rev., *22*, 117, (1906.)
[5] Report of the Brit. Ass., p. 39, (1904).

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is of little importance; but when it comes to a question of a standard of E. M. F., it is not to be overlooked. The rate of this change seems to be more rapid at higher temperatures, and especially does the depth of the paste in the cathode leg of the cell play an important role in the rate of the change. Some cells were made in November, 1904, and the paste was only 3 or 4 mm. deep. The object was to make a cell with a smaller internal resistance. These (N) cells showed the value 1.01844 when first compared, but by January, 1905, were 1.01839, and on April 4, 1905, were 1.01811 v., while by June, 1905, they were down to 1.01767, and had become very irregular. It is noticeable that the (F) cells are no longer in as good agreement as they were when first constructed. The paste in the (F) cells is about 10 mm. deep, and in the new (A) cells it is 20 mm. deep. It might be added that these (A) cells have not yet shown a change, but it is probably only a question of time.

A number of observations, made on the cadmium cells during the last two years, are in harmony with the idea that the system in the cathode leg of the cadmium cell is not in equilibrium. The attempt to simplify the construction of the cadmium cell by electrolytically forming the depolarizer in the cell after it had been set up,[6] was a complete failure, and since then, mercurous sulphate was made electrolytically from a saturated cadmium sulphate solution and a mercury anode; the solution was rapidly stirred and two different current densities were used, but the cells in which these samples were placed when tested, did not agree and are not satisfactory. It was expected that this would give a product which was in equilibrium with the cadmium sulphate solution, and that the manipulations incident to the washing and making the paste would be avoided.

In order to test further this system of the cathode leg of the cadmium cell, the following experiment has been tried. An adjustable cadmium cell was first made; the side tube of the cathode leg of this cell bends down and passes into the top of the tube which holds the mercury, paste, and cadmium sulphate of the cathode leg. This adjustable cell has shown a constant value of 1.01837 at 25°, and the anode leg may be removed to test other cells or systems. A large tube, closed at one end and

[6] Hulett, Phys. Rev., *22*, 50 (1906).

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with a narrow neck at the other, was filled with the system—mercury, mercurous sulphate, cadmium sulphate, and saturated solution—this tube was slowly rotated about its longer axis in a 25° thermostat. From time to time, this tube was brought to an upright position, the cork removed, and the contents tested with anode leg of the adjustable cell. Contact with the mercury of the large tube was made by means of a platinum wire which had been fused through the closed end of the tube. Care was taken to protect the rotating tube from the light, and other necessary precautions were taken. After rotating thirteen hours, the system was tested, and the value 1.01764 v. obtained. The E. M. F. was not constant but decreased on standing. This variation was largely due to the mercury being in a finely divided state, evidently the tube had been rotated too rapidly, therefore the subsequent rotation was sufficiently slow to allow the mercury to remain in one large globule. After three and one-half days, the value of 1.01941 v. was obtained. In fourteen and one-half days, the value was 1.01971 v., and in twenty-one days, the value was 1.01990 v. The system is still changing, and is now .00140 v. higher than the cadmium cell. When this system becomes constant, the mercurous sulphate will be tested in a cell. Meantime, the same experiment has been carried out with the cathode system of the Clark cell. An adjustable Clark cell was made and has shown a constant value of 1.42045 volts at 25°. The system—mercury, mercurous sulphate, zinc sulphate, and saturated solution—was rotated in a tube as described above, first for twelve hours, and when the anode leg was adjusted, the value 1.42046 v. was obtained. After six days, the reading was 1.42050 v., and after seventeen days, the E. M. F. was 1.42052 v. This severe test shows that the system of the cathode leg of the Clark cell comes to equilibrium in a short time, and that further change is not to be feared. The slight increase noticed may be due to the effect of light on the rotating system, as no special precautions were taken to avoid diffused light in the thermostat.

The results of the experiments here recorded are distinctly in favor of the Clark cell as a standard of E. M. F. The conclusion that the system in the cathode leg of the cadmium cell, as at present constructed, is not in equilibrium, and that the E. M. F.

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of the cell does change with time, clearly follows from the experimental results. Attention might be called to the low values for the (F) cells on August, 1905, and the higher value for December, 1905. Between these two dates, the (D), (F), and old (H) cells were taken from Ann Arbor, Mich., to Princeton, and while they were very carefully carried, the jarring may have effected this change. Some other experiences indicated this same thing, and it is in harmony with the results with the rotated system.

It is to be noted that on rotating the cathode system of the cadmium cell, the E. M. F. of the cell increases and becomes very much greater, while the cell shows a slowly-decreasing value of its E. M. F., so that the above experiment, instead of explaining the "drift," has stirred up more trouble. It is hoped that further work will explain the results obtained and suggest a remedy for the "drift," as the low temperature coefficient of the cadmium cell is an exceedingly desirable feature, and with the electrolytic mercurous sulphate as depolarizer, the cell seems to be reproducable to one or two parts in 100,000; but cells should be made every few months to detect the presence and magnitude of the "drift." If the paste is over 15 mm. deep in the leg of the cells, the change will be very slow. The cell has a value of 1.01843 v. at 25°, and follows the accepted coefficient very exactly.

The Clark cell, with electrolytic mercurous sulphate as depolarizer, is nearly as reproduceable as the cadmium cell and it retains its value. Some experiments are being concluded which indicate that this cell may be simplified and made even more reliable. The Clark cell, with electrolytic mercurous sulphate as depolarizer, has its constant value at once, and is 1.42040 v. at 25°, or 1.43300 v. at 15°. The temperature coefficient is over a millivolt per degree, and for accurate measurements, the temperature must be known to 1/100 degree.

Princeton University,
April, 1906.

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DISCUSSION.

PROF. W. LASH MILLER: If I understand rightly, when zinc is replaced by cadmium, the E. M. F. changes on standing or shaking. Could that possibly be due to any action of the glass? Owing to the difference of strength of zinc as a base, and cadmium as a base, there would be slightly more acidity in one case than in the other; and the glass might dissolve more readily in the cadmium solution.

PROF. HULETT: Of course attention has been given to impurities, and I might say that ordinary impurities, with the exception of sulphuric acid, have very little effect on the E. M. F. of these cells. If the solution in the cell is acid the E. M. F. is low, but one cell in which some cadmium hydroxide in excess was used, had the same value as the normal cells, and as the hydroxide has a noticeable solubility in the cadmium sulphate solution, it is hardly to be expected that the small amount of alkali from the glass would have a measurable effect.

PRESIDENT BANCROFT: Then, as I understand it, the change is in the sense that it would be if the cadmium sulphate became slightly acid in time.

Evidently, the difficulty is not in the mercurous sulphate and mercury by themselves; therefore it must be either a difference in the solubility,—in the absolute solubility of the cadmium sulphate, in the quickness with which it reaches equilibrium, or in the stability of the cadmium sulphate.

PROF. HULETT: If sulphuric acid is formed in the cell it would account for the "drift," since, as already mentioned and as shown by Kahle, the presence of sulphuric acid in the cell lowers the E. M. F. If the cadmium sulphate solution should hydrolyse the mercurous sulphate and form an insoluble basic a soluble acid salt, the acid salt would diffuse to the amalgam of the anode, lose its mercury, and leave the acid. This process would continue and slowly increase the acid concentration in the cell with the result of slowly decreasing the E. M. F. This interesting possibility has been tested by examining the solutions from some old cells. An H cell with cadmium amalgam in both legs was used, in one leg was the saturated solution of cadmium sulphate, while the other contained this solution to which

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a known amount of acid had been added. It was found possible to detect one part of acid in 10,000 parts of the saturated solution, but I have not been able to detect acid in the solutions taken from the old cells. It would require a decidedly measurable amount of the acid to account for the low value of these cells, if that was the cause.

MR. PATTEN: I would like to bear testimony to the excellence and accuracy of Dr. Hulett's description of his method. Prof. Augustus Trowbridge and I last summer made up about 24 of these cells and were highly pleased with the results and with their constancy. I do not remember the exact figures; but about ten to fifteen maintained their constancy, some I think to within one part in 100,000. Prof. Trowbridge carried two cells to the Reichsanstalt, had them standardized, and brought them back. He still has the cells at Wisconsin, and I suppose their records are very accurately laid out and available.

PROF. HULETT: Did you find any difference in the E. M. F. of the cells after they were brought back?

MR. PATTEN: I have not seen Prof. Trowbridge recently, but he has the set of cells which he brought back, two of them; he has them there and it can very readily be determined.

PROF. HULETT: This is an interesting point. One of the D cells was taken to the Washington meeting by Prof. Carhart, but when the cell was returned it was found to be .00004 volt higher than the other D cells and remained that way for a long time. Evidently the jarring due to travelling affects the E. M. F. of the cadmium cell. You will see in the table that the D and F cells were distinctly lower in Aug. '05 than in Dec. '05. Now these cells were made in Ann Arbor, Mich., and transported to Princeton between those two dates. This agrees with some work now being completed which indicates that the system in the cathode leg of the cadmium cell is not a system in equilibrium, and it would be very interesting to know whether the cells taken to Europe by Prof. Trowbridge behaved similarly.

PRESIDENT BANCROFT: All work like this on the primary standards is of the very greatest importance; we are very much indebted to Mr. Hulett for the presentation of this paper; and we hope that another year he may be able to tell us what the cause of the ageing is in the case of the cadmium sulphate cells.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

ELECTROLYTIC PRECIPITATION OF BRONZES.

By B. E. CURRY.

It is commonly supposed that it is difficult to precipitate good bronze electrolytically. For this reason the general method for preparing bronze plate is to precipitate a brass and bronze it by chemical methods[1].

The best brass is precipitated from cyanide solutions. Because of the slight solubility of the cyanide of tin this solution cannot be employed for the deposition of bronze.

Brass cannot be precipitated satisfactorily from ordinary salt solutions. The tendency for the copper to precipitate first causes the solution to concentrate continually with respect to zinc and at the same time to become poor in copper. When the ordinary salt solutions of copper and tin are electrolyzed the copper precipitates first and the solution becomes rich in tin. For this reason the more common electrolytes cannot be used for a continuous precipitation of bronze.

Since the ordinary salt solutions are not satisfactory for the deposition of bronze it was thought advisable to try some solution in which both copper and tin form soluble double salts. In selecting an electrolyte the behavior at the anode as well as at the cathode must be considered. It has already been shown that over a considerable range the bronzes dissolve quantitatively[2] in both alkaline tartrate and acid ammonium oxalate solutions.

Some tests with the alkaline tartrate solutions showed these to be undesirable. A satisfactory bronze could not be obtained and the solution changed continually in concentration. In the presence of the stannous salts the copper was thrown from solution and deposited on the walls and bottom of the containing vessel. For these reasons the tartrate solution was abandoned.

Some preliminary tests with acid ammonium oxalate solutions,

[1] Watt and Philip, Electroplating of Metals, 308.

[2] Electrolytic Corrosion of the Bronzes, Trans. Am. Electrochem. Soc., 9, (1906).

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produced a good bronze. Experience has shown that this solution must be prepared with a considerable amount of care. If the acid content is made too high the copper is precipitated as an insoluble salt. When the acid content is too low or the solution slightly alkaline the tin becomes insoluble. At ordinary temperatures about 7 per cent. oxalic acid forms a saturated solution; the ammonium salt is a little less soluble.

It was noted early in the work that there was a wide difference between the composition of the deposited bronze and the relative amounts of copper and tin in solution. In order to determine the composition of the solution and that of the bronze the following stock solutions were prepared:

Grams $H_2C_2O_4$	Grams $(NH_4)_2C_2O_4$	Grams $CuSO_4\,5H_2O$	Grams SnC_2O_4	H_2O
5	55	——	18	1000 cc
5	55	15	——	1000 cc

From these, two series of solution were made up with known amounts of copper and tin varying in shifts of 10 per cent. It will be noted that these solutions are different from the solutions in which the corrosion experiments were made, inasmuch as they contain sulphates. The presence of sulphates or chlorides is necessary in order to keep the copper in solution. One of these series was electrolyzed with a 90 per cent. copper anode and the other with an 80 per cent. anode. In each case about 0.3 gram of bronze was deposited, weighed and then analyzed. The anodes were weighed before and after each run. In this way a check was had on the composition of the solution at the end of the run. In runs of this length the total change in the concentration of the copper and tin in solution was not great. Corrections were calculated for this and the results plotted in Fig. 1. Here the coordinates are percentage copper in solution and percentage copper in the precipitated bronze. As the curve indicates that there is a wide difference between the composition of the solution and of the precipitated bronze, the curve also indicates that the lowest copper content an electrolytic bronze can have is about 78 per cent. However when a 75 per cent. copper anode is used, a fairly good bronze with 75 per cent. copper content can be obtained. When the copper content in solution becomes as low as 10 per

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cent of the total amount of copper and tin in solution, same care is necessary to prevent the deposit from becoming black and spongy. Also the composition is likely to vary.

In these runs the anodes were cast in the form of plates with a surface on one side of about 40 cm^2. The cathodes were platinum discs with a surface of 30 cm^2. The cathodes were rotated and in this way the solutions kept well stirred and the deposit remained bright and smooth. If the solutions are not stirred the deposits blacken very quickly. If the anodes remain stationary there is some tendency for slimes to form, but this is not great.

In order to show more conclusively that the curve in Fig. 1 represents the facts obtained in longer runs, solutions containing relatively 82.5 per cent., 70 per cent. and 60 per cent. copper were

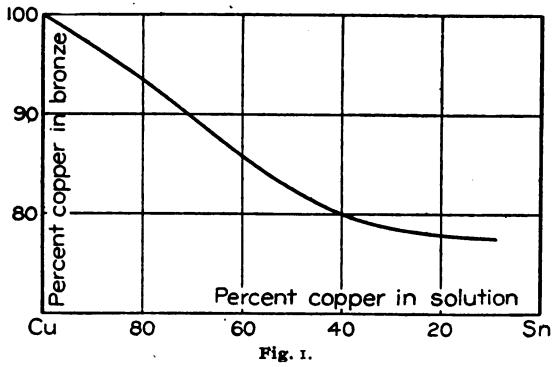

Fig. 1.

electrolyzed with 95 per cent., 90 per cent and 85 per cent. copper anodes respectively. The anode density was 0.3 ampere per sq. dm. and the cathode density 0.2 ampere per sq. dm. In this case the cathodes were cast in the form of cylinders and both cathode and anode were rotated. At the end of the run both the anode and cathode were bright and clean. The results are given in Table I.

TABLE I.

Per cent. Cu in anode.	Per cent. Cu in solution.	Anode loss in grams.	Wt. of bronze in grams.	Per cent. Cu in bronze.
95	82.5	3.44	3.51	94.7
90	70.0	2.70	2.52	89.5
85	60.0	3.08	2.90	86.5

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At the end of the runs about 0.3 grams of the bronze were deposited on clean electrodes and analyzed. In the solutions which were electrolyzed with 95 per cent. and 90 per cent. copper electrodes, the solutions were practically unchanged. The 85 per cent. anode became tin-rich on the surface and for this reason the concentration of the solution and deposited bronze shifted slightly. The bronzes with a copper content varying between 74 per cent. and 87 per cent. are composed of two phases, the α phase rich in copper and the δ phase richer in tin. In oxalate solutions containing sulphates the α phase tends to dissolve first and the surface of the anode becomes rich in δ crystals. Between 87 per cent. and pure copper the bronzes have but one form of crystallization and dissolve uniformly without change.

A second series of runs was made with copper chloride substituted for the copper sulphate in the original solution. The chlorides do not interfere with the cathode reaction in any way. The results are given in Table II.

TABLE II.

Per cent. Cu in anode.	Per cent. Cu in solution.	Anode loss in grams.	Wt. of bronze in grams.	Per cent. Cu in bronze.
85	60	2.01	2.37	85.5
80	49	2.38	2.00	81.2

These anodes dissolved without change and the tendency to dissolve tin-rich did not appear as in the solutions containing sulphates.

In these longer runs the deposits remained bright but became rough and pitted toward the end.

Some experiments were made with a high current density at the anode to determine the effect on the solubility. With a current density of one ampere per square decimeter the anodes containing more than 87 per cent. copper dissolved uniformly and with a good efficiency. With less than 87 per cent. copper at the higher current densities the tendency for the anodes to become tin-rich was more apparent. The current density at the cathode can vary over a considerable range and the deposit remain satisfactory. Good deposits were obtained with a current density varying from 0.2 amperes to 2 amperes per square decimeter.

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When cast bronzes with more than 87 per cent. copper are annealed below 500°, they are homogeneous under the microscope. There is but one form of crystallization over this range. These crystals are designated as α. The bronze with 74 per cent. copper is also homogeneous and this particular form of crystallization is designated as δ. Over the range between 74 and 87 per cent. copper, the bronzes are not homogeneous but show a mixture of α and δ crystals.

It is certain that the electrolytic bronzes are deposited under equilibrium conditions. All of these appear homogeneous under the microscope when the copper content is above 90 per cent. The 76 per cent. copper bronze is almost homogeneous but there is evidence of a small amount of a second phase. The 83 per cent. bronze shows two phases in almost equal amounts.

The electrolytic bronzes with more than 88 per cent. of copper bend readily but with a less amount of copper the bronze begins to harden and break when bent. These do not dissolve readily in nitric acid. The electrolytic bronzes correspond closely in color and general appearance to the cast bronzes over the same range of composition.

The best plating solution for bronzes should contain about 5 grams of free oxalic acid and 55 grams of ammonium oxalate per 1000 cc. water. The relative amounts of copper and tin in solution may be shifted in any ratio depending on the composition of the plate desired. The cathode should be rotated if possible.

The presence of chlorides is preferable to large amounts of sulphates.

It has been found to be very difficult to precipitate a good bronze with less than 75 per cent. copper content.

A low current density at the cathode is necessary.

The anode dissolves better when rotated.

The electrolytic bronzes represent equilibrium conditions.

This work has been carried on under a grant from the Carnegie Institution to Professor Bancroft.

Cornell University.

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DISCUSSION.

PROF. W. LASH MILLER: Were experiments made to see whether the bronzes as desposited were in a state of equilibrium? The bronze containing 80 per cent. of copper, for instance, if in equilibrium would consist of a mixture of Alpha and Delta; were any corrosion experiments made to test this?

MR. CURRY: I found, in dissolving these bronzes, that they were very difficult to dissolve. A microscopic examination shows that the electrolytic bronzes are in a state of equilibrium.

PRESIDENT BANCROFT: There is one point, that is of interest here. If you have a 90 per cent. anode and are depositing a 90 per cent. bronze from it, then barring accident the solution remains entirely unchanged and you have apparently a completely reversible state of things. As a matter of fact it is not reversible theoretically for this reason, that the composition of the bronze which is precipitated electrolytically depends on the relative amount of copper and tin in the solution. The corrosion of the anode is quite independent of the relative amounts of copper and tin, always supposing, of course, that you have not got so much that the copper precipitates directly on the anode; in other words, the corrosion of the anode depends primarily on the anion in the solution. The precipitation at the cathode depends primarily on the relative concentrations of the copper and tin as ion; so that the anode process and the cathode process are not strictly reversible, even though analytically they may give exactly the same results.

PROF. MILLER: If there were no decomposition voltage, that is if a current could be sent from one piece of bronze through the solution to the other without polarization, then in the thermodynamical sense the reaction would be reversible.

PRESIDENT BANCROFT: Possibly.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

FERROMANGANESE ANODES IN CAUSTIC SODA SOLUTIONS.

By G. R. White.

Lorenz[1] has shown that potassium permanganate is formed when ferromanganese is made anode in a dilute caustic potash solution. On repeating this experiment with varying conditions, the green manganate was often obtained. It looked as though this was a case in which the nature of the product varied markedly with varying conditions. In the fifth American edition of Richter's Inorganic Chemistry, page 391, it is stated that the red permanganate solution changes to the green manganate on addition of an alkaline hydroxide. Assuming this to be true, the favorable conditions for the manganate would be a concentrated alkali and a high temperature. Since the valency of manganese is higher in the permanganates than in the manganates, it might be thought that a high anode density would favor the formation of the more highly oxidized substance, the permanganate. This last assumption is of doubtful accuracy, but the experiments apparently confirmed all the predictions. Cast ingots of ferromanganese, with a surface of approximately 10 cm^2, were used with platinum wire cathodes. With a 2 per cent. solution of sodium hydroxide, made from "pure sticks," and a current of 1.25 amperes, permanganate was formed when the electrolysis was carried on at ordinary temperatures. With a 10 per cent. solution and a current of 0.25 amperes, manganate was obtained. At 90°, manganate was formed under all conditions of concentration and current density. While this was apparently very satisfactory, there were some facts which did not fit in. Under all circumstances, there was a layer of red solution immediately in contact with the anode. This made it appear as though the ferromanganese always dissolved as permanganate, in which case the formation of manganate would be a secondary reaction having nothing to do with the electrolytic phenomena. When a current

[1] Zeit. anorg. Chem. *12*, 393 (1896).

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of 1.25 amperes was run through a 10 per cent. caustic soda solution for an hour and a half, the green color changes gradually to the pink permanganate. On the other hand, it was noticed that an alkaline solution of permanganate becomes green if allowed to stand over night in an open beaker. These apparent contradictions disappear if the statement in Richter's is wrong, and if the following quotation from Roscoe & Schorlemmer[2] is right:

"The permanganates are converted into manganates with evolution of oxygen when their solution in concentrated caustic potash is boiled:

$$\text{"}2KOH + KMnO_4 = 2K_2MnO_4 + O + H_2O.$$

"The same change occurs when reducing agents, such as alcohol and sodium thiosulphate are added to the solution, only so much, of course, being added as suffices for the reduction of the permanganate to manganate. The red alkaline solution turns blue and afterwards green on exposure to the air, this being caused by the reducing action of the *organic matter*[3] contained in the atmosphere."

No experiments have been made to determine how concentrated the caustic potash must be in order to cause the permanganate to break down when the solution is boiled; but the reaction does not take place with 50 per cent. caustic soda. One thing, however, is certain, and that is that organic matter or other reducing substances are necessary for the reduction of permanganate to manganate in alkaline solutions at temperatures up to 100°.

The change on standing over night is to be explained as follows: The solution contains only a relatively small amount of permanganate, and is strongly alkaline. Under these conditions, organic dust particles falling into the open beaker, bring about the reduction to the manganate:

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + [O]$$

The fact that a green color is produced in all cases on diffusion of the permanganate into the electrolyte indicates that the electrolyte contains organic matter, and this view is confirmed by the fact that the green color persists longer in the concentrated than in the dilute and disappears sooner when the current is high, or

[2] Vol. II. Part II. Pg. 19 (Edition 1886).
[3] Italics are mine.

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in other words, when the amount of permanganate being formed is relatively large.

Assuming then that organic matter is necessary for the reduction of the permanganate to manganate, an effort was made to overcome this contamination as much as possible. In the first place, up to this time the beakers in which the electrolysis was carried on were covered with wooden electrode holders. Inasmuch as hydrogen was given off at the cathode and oxygen at the anode, it was thought that these gases might tend to carry the alkali mechanically up to the cover, the sodium hydroxide would then act on the cover, and, sooner or later, drop back into the electrolyte, laden with organic material. Furthermore, the base might attack and weaken the wooden cover so that particles of wood might drop into the solution. Any organic matter thus introduced would most certainly aid in the formation of the manganate. For this reason, glass covers were substituted for the wooden, in the subsequent experimental work. Again, it was found that with commercial sodium hydroxide, the green color persisted much longer than with a better grade of the alkali—the commercial, doubtless, being more contaminated with organic matter because of careless handling.

Therefore, in order to rid the electrolyte of any organic matter, it was decided to add enough permanganate to make the solution pink. With this precaution, it would be safe to assume that the electrolyte was free from any organic material. Runs were made, using the same current strengths and the same concentrations as before. The 2 per cent. solution, with 0.25 and with 1.25 amperes, started pink and remained pink after running for two hours, in each case. Likewise, the 10 per cent. solution, with the same current strengths as above, remained pink after a similar period of time. For this reason, it seems very probable that the production of anything but permanganate at ordinary temperatures is due entirely to the presence of some reducing agent in the solution.

The question now comes up, "How may we explain the fact that the permanganate, on standing over night, becomes green?" In answering the question, it must be remembered that after all the organic or other reducing agents have been removed, it requires only a very small quantity of permanganate to give the

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solution a pink color. Furthermore, some time is required before the reaction

$2K_2MnO_4 + 2KOH$ containing organic or other reducing agents $= 2K_2MnO_4 + 2H_2O + [O]$

comes to equilibrium. No study has been made of the exact speed of this reaction, but from cursory observations, it is noticed that at first the reduction goes on rapidly and completely, but gradually slows down and requires time for the final equilibrium to be reached. The experiments at first performed were run just long enough to give a definite permanganate color all through the electrolyte. Then on standing for a time (usually over night), it was found to be green in the morning. The explanation for this is that the amount of permanganate in the electrolyte was relatively small, that the solution was still strongly alkaline, and that the reducing reaction had not come to equilibrium. Although the concentration of the organic or reducing agents was low, it was still effective, and therefore required time to come to complete equilibrium with the final production of the green manganate. Furthermore, it is more than likely that the introduction of organic dust particles from the air aided in some measure, but this is not such a tremendously important factor, and is effective only when the solution is extremely alkaline.

An experiment was tried to prove this explanation, *i. e.*, that if the permanganate were present in sufficient concentration, it could not be reduced to manganate on standing for a short time. A 10 per cent. solution of sodium hydroxide was taken with ferromanganese as anode and a platinum wire cathode as before, and a current of 1.25 amperes was passed through the electrolyte for six hours. The usual phenomena were observed—permanganate formed at anode, reduction to manganate on diffusion, and the gradual disappearance of the manganate as the electrolysis progressed. On breaking the circuit, the solution was so deeply colored by permanganate that its color could not be judged by transmitted light. This solution was left over night, and in the morning it was still colored with permanganate, and, although still strongly alkaline, the permanganate color persisted for four days. This solution was allowed to stand in an open beaker, which seems to show that the greatest part of the organic or reducing agents were removed from the electrolyte, and that the

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permanganate was reduced only very slowly by the organic dust particles.

The conditions of concentration and current strength have been taken up, and it has been shown that neither have any effect on the production of permanganate, so it was decided to try the effect of temperature. The higher temperatures are especially favorable to the formation of manganese compounds of a lower valency. As an instance, when a salt of manganese, the valence of which is less than six or, according to Ostwald, of any valence, is fused with K_2CO_3 or KOH and KNO_3, the manganese is oxidized to K_2MnO_4, and not $KMnO_4$. In this fusion, as in the case at hand, it is alkaline conditions with which we are dealing, although the results are different, for in one case manganate and in the other permanganate is found. While the temperature difference between the fusion and 95° (at which temperature the electrolysis was carried on) is wide, still it serves as an indication of the way in which the electrolysis might be expected to go at the latter temperature, 95°. The electrolysis of both the dilute and concentrated electrolytes with both current strengths, even though the electrolyte was first made pink with permanganate, gave the green manganate after running about half an hour. The beaker was covered with glass, the thermometer in the electrolyte preventing complete covering, but the vapor issuing from the beaker would greatly reduce the possibility of the introduction of organic matter from the air, which, moreover, has been shown to be of minor importance in *rapid* reduction. At this temperature, 95°, there is a strong tendency to form ferrates, especially with the concentrated solution. It was thought at first that the reduction might be due to the reduction of the ferrates to ferrites by hydrogen at the cathode. Against this supposition, Haber and Pick have observed that the amount of this reduction is trifling. However, that there is dissolved iron present in the solution is indicated by the fact that iron is precipitated on the cathode. This iron is also noted in the cold solution, but no reduction of the permanganate takes place. Analysis of the electrolyte after reduction had taken place showed iron, and, furthermore, analysis of the sodium hydroxide used as electrolyte also showed iron. It is therefore not safe to conclude that the reduction is due to the formation of ferrates, which are reduced to ferrites by hydrogen for three reasons:

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First—According to Haber and Pick, the amount of reduction from ferrate to ferrite is small.

Second.—Iron is precipitated on the cathode at both 95° and at room temperature, yet no reduction is noted in the solutions at room temperature.

Third.—The electrolyte contains iron *before* as well as after the electrolysis.

The reduction, then, must be due directly to the hydrogen at the cathode. This can be proved as follows: A porous cup was boiled out in alkaline solution of permanganate to rid it of reducing agents, then with dilute hydrochloric acid, to rid the pores of manganese dioxide, and finally, again with dilute alkaline permanganate, to get rid of the acid. This cup was then made the cathode compartment of a cell which contained a 2 per cent. solution of sodium hydroxide, made pink with permanganate and heated to 95°. The cathode was a platinum wire, the anode was ferromanganese, as before, and a current of 1.25 amperes was used. The solution in the cup was reduced to manganate in less than eight minutes. The electrodes were then reversed—the ferromanganese anode being placed in the cup (the solution in cup was still green) and the platinum cathode placed outside. In sixteen minutes, there was complete reduction to manganate, more time being required because the amount of solution was greater. The electrodes were again reversed, cathode now in the cup, and in about seven minutes the reduction was complete. The electrodes were then reversed again, with the result that reduction took place in a few minutes. This shows that the reduction is due to the hydrogen at this temperature. Furthermore, it was found that hydrogen from a Kipp easily reduces an alkaline permanganate.[4] The reduction takes place slowly at room temperature, and much more rapidly when heated to boiling.

The equation for this reaction is represented as follows:

$$2KMnO_4 + 2KOH + H_2 = 2K_2MnO_4 + 2H_2O.$$

Thus it is seen that the chemical and electrochemical reactions are in strict accord.

Thénard[5] said that the reduction of permanganate to manganate

[4] Jones, Jour. Chem. Soc., *33*, 95 (1878).
[5] Jour. prakt. Chemie, *69*, 58 (1856). Comptes rendus, *42*, 382 (1856).

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took place only with an alkali which contained some oxidizable substance. When the solution was made pink before running the current through the electrolyte, no formation of a manganate was noticed. However, if to an alkaline solution of permanganate alcohol is added, the permanganate is immediately reduced to manganate, and the odor of aldehyde is apparent. If the reaction

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + [O]$$

is considered, it will be noted that oxygen is given off. An experiment was tried to see whether or not this was the case. Some alkaline permanganate solution was placed in a cylinder, which was fitted with a rubber stopper, through which ran a glass tube, at the upper end of which was a Bunsen valve. The level of the liquid in the cylinder and tube was marked. This cylinder has stood three months, is still highly colored with permanganate, and the levels have not changed. Furthermore, the cylinder was heated in a bath to 95°, and after cooling down, the levels were not altered. These results show that under these circumstances a gas is not given off.

From the results of some preliminary experiments made on the action of sodium hydroxide on permanganate, it was decided to try the effect of various amounts of sodium hydroxide, colored with permanganate, on various amounts of permanganate.

A series of sixteen beakers was made up of 150 cc. mixtures of the alkali and permanganate. The alkali was a 10 per cent. solution, and the permanganate a 1-10 per cent. solution. The first beaker had 5 cc. of the alkali and 145 cc. of the permanganate. The number of cubic centimeters of permanganate was decreased by 10 cc. steps, beginning with 140 cc., and the alkali increased by like amounts, until the number of cc. of sodium hydroxide reached 140 cc., then the increase and decrease was reduced to 5 cc. Thus the first beaker contained 145 cc. of permanganate and 5 cc. of sodium hydroxide; the second, 140 cc. of permanganate and 10 cc of sodium hydroxide; the third, 130 cc. of permanganate and 20 cc. of sodium hydroxide, and so on down, until the next to last contained 10 cc. of permanganate and 140 cc. of sodium hydroxide, and the last 5 cc. of permanganate and 145 cc. of sodium hydroxide. Under these circumstances, it may be inferred that any reduction to the manganate is due almost entirely to

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the introduction of organic matter from the atmosphere. The first to change was the one containing the 145 cc. of sodium hydroxide, and the change was noticed six days after the experiment was started. The second to become green was the one containing 140 cc. of sodium hydroxide, which turned green eight days after beginning the experiment. Up to the time of writing, six out of the sixteen have turned green, the change taking place in order of the amount of alkali present. Owing to the fact that they are standing in open beakers, the amount of evaporation is large, and the concentration is therefore changing. The evaporation is uniform, however, so the relative concentration is not changed. At points where the solid has crept up the sides, a reduction is noted, and is due, no doubt, to the better chance which the more concentrated solution has of attracting the dust particles.

Another experiment was tried to show the effect of surface exposed on the rate of reduction. A solution of known strength of permanganate was treated with a known quantity of 10 per cent. sodium hydroxide (which had been made pink with permanganate) and divided into two equal portions. One of these portions was placed in a beaker and the other in a crystallizing dish, the ratio of the surface exposed being 1 to 14. The solution in the crystallizing dish was reduced in less than a day, while the solution in the beaker is still unchanged at the time of writing. This is another striking instance of the effect of organic dust in reducing, also the effect of increasing concentration. These results seem to indicate that the dust from the atmosphere will reduce, if given sufficient time, especially if acting in a concentrated solution.

What then can be said of the reaction:

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + [O].$$

At room temperatures and temperatures up to 95°, with a concentration at the start of 10 per cent., sodium hydroxide, permanganate is not reduced by sodium hydroxide which is free from organic or reducing agents. When reducing agents are present, no gas is evolved, because the oxygen immediately combines with the reducing agent. Therefore, working within the concentrations stated, it is safe to say that the above equation

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does not represent the true state of affairs—the permanganate is not reduced to manganate by sodium hydroxide alone, and that even when reduction does occur no gas is evolved. The above statement holds only for the concentrations and temperatures mentioned.

1.—Permanganate is formed at both concentrations of alkali used (2 and 10 per cent.), irrespective of the current strengths (0.25 and 1.25 amperes).

2.—At 95°, it is reduced by hydrogen to the green manganate.

3.—Any reduction at ordinary temperatures is due to reducing agents in the electrolyte.

4.—The chemical and electrochemical results are in perfect accord.

The work was suggested and carried out under the direction of Professor Bancroft.

Cornell University.

[*Added June 15th.*]

It was found that the order in which the alkaline solutions of permanganate changed to the manganate followed exactly the order of increase in the alkalinity. As indicated above the more alkaline solutions were the first to change. However the first four beakers containing respectively 145 cc of $KMnO_4$ and 5 cc of alkali; 140 cc of $KMnO_4$ and 10 cc of alkali; 130 cc of $KMnO_4$ and 20 cc of alkali; and 120 cc of $KMnO_4$ and 30 cc of alkali, are still pink. These four beakers have stood three months already and are still pink although some manganese hydroxide has precipitated out on the glass, indicating a slight reduction. This shows conclusively that the reduction in alkaline solutions depends on two factors—the alkalinity and amount of reducing material present.

In the electrolysis it was noted that a large quantity of gas was evolved at the anode and it was therefore suspected that the efficiency was low. On testing, the maximum efficiency found was only 12 per cent. To determine the amount of permanganate formed the electrolyte was made acid by adding H_2SO_4 and then titrated with standard oxalic acid.

An attempt was made to ascertain the manner in which the permanganate was formed from the manganese. Is a hydroxide or oxide formed first and then oxidized to the permanganate? If

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manganese precipitated on copper from a concentrated $MnCl_2$, is made anode in sodium hydroxide the manganese forms permanganate at once with a current of 250 milliamperes. With a current of 50-75 milliamperes the permanganate is formed very slowly and with a current of 5 milliamperes no permanganate is visible until such a current has run for 12 hours. On the other hand with ferromanganese as anode, permanganate is formed at once with all current strengths.

On exposure to the air the freshly deposited manganese becomes coated with a film of oxide or hydroxide. This hydroxide cannot be oxidized electrolytically to permanganate. If $Mn(OH)_2$ is spread over a platinum or nickel electrode and is made anode in sodium hydroxide it oxidizes to the black MnO_2 when a current of 2 or 3 amperes is passed through the electrolyte and no further oxidation is noted. Furthermore if a piece of MnO_2, suspended by winding a platinum wire around it, is made anode in sodium hydroxide no further oxidation occurs either at room temperature or at 120° with two current strengths of 3 or 14 amperes. The same thing holds whether a 2½ or a 50 per cent. solution of sodium hydroxide is used as electrolyte and also when a very small amount, 50 milliamperes, is passed through the 2½ per cent. electrolyte for 10 hours.

The normal reaction between manganese and caustic soda involves the formation of manganous hydroxide. When the current density is raised sufficiently, the formation of manganous hydroxide and of permanganate goes on simultaneously. Ferromanganese has practically no tendency to decompose water or caustic soda solution and therefore the only reaction is the formation of permanganate. The permanganate formed when manganese is made anode for a long time with a low current density cannot come from the manganous hydroxide. The last portions of the manganese to dissolve must therefore be in a different state from that which dissolves first. The last portions of the manganese to dissolve are those in immediate contact with the copper wire and it is probable that we have here a slight formation of cupromanganese, analogous to the formation of the zinc-platinum alloy when zinc is precipitated upon a platinum cathode. Special experiments with cupro-manganese show that it behaves like ferromanganese and forms permanganate even with low current densities.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

THE SETTLING OF SUSPENSIONS.[1]

BY EDGAR BUCKINGHAM.

The following paper contains an account of some experiments on the settling of suspensions in various liquids, together with certain theoretical considerations bearing on the results. The experimental part is to be regarded merely as an outline sketch to be filled in later, when the theoretical part may have to be changed if the future experiments show that the generalizations from these few experiments have been premature. On account of the preliminary nature of the paper, references to the literature have been omitted.

§ 1.—The suspensions used, were: (a), quartz flour in various states of fineness, containing probably small amounts of steel and porcelain, since the quartz was ground in a porcelain mill with steel balls; (b), rutile (TiO_2) ground in the same way and with similar impurities; (c), several agricultural soils containing a large proportion of very fine particles. A very few experiments were also made with lead carbonate, tourmaline, and hematite.

The liquids used are those named in the table, together with several mixtures and solutions in which they acted as solvents. The liquids were commercial, and were not purified or tested as regards purity. The values given for the physical constants are for temperatures between 15° and 23°. Closer specification is unnecessary, as will appear presently:

Liquid	Surface Tension (C.G.S.) T	Density ρ	Viscosity (C.G.S.) η	Specific Conductance K	Dielectric Constant $\lambda=\alpha$ D.C.
Water	75	1.0	0.0100	—— ——	81.
Alcohol, 95% . .	22	0.82	0.0144	7 to 14 × 10^{-6}	26.
Acetone	24	0.80	0.0032	12 × 10^{-6}	25.
Amyl alcohol .	24	0.81	0.0400	2.2 × 10^{-7}	16.
Aniline	44	1.02	——	9 × 10^{-8}	7.3
Ethyl acetate .	24	0.90	0.0044	1.9 × 10^{-6}	6.1
Chlorofom . . .	26	1.5	0.0055	5 to 16 × 10^{-11}	5.2
Ether . . .	17	0.73	0.0024	5 to 30 × 10^{-10}	4.3
Carbon bi-sulfide	33	1.26	0.0039	2 to 5 × 10^{-12}	2.6
Benzene	29	0.88	0.0058	1.5 × 10^{-13}	2.3
Toluene	28	0.89	0.0056	> "	2.3
Xylene	29	0.88	0.0062	"	2.4

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The surface tensions, densities, and dielectric constants are taken from the tables of Landolt and Börnstein. As they are the values for pure liquids, while the liquids I have used were not specially purified, the values are to be regarded as only approximate.

The viscosities I measured by the capillary tube method, taking the value for water as known. They agree, in all cases, with the values given by Thorpe and Rodger for the same temperatures, within a few per cent., (within 2 per cent. in half the cases) being generally somewhat larger than Thorpe and Rodger's values.

The conductivities which are expressed in reciprocal ohms per cubic centimeter, were measured, (a), with alternating current and the Wheatstone bridge for $K > 10^{-7}$; (b), by direct deflexion of a galvanometer for $K < 10^{-7}$. The water used was not very pure, having a conductivity of from 20 to 40×10^{-6}

It will be noticed that the liquids are arranged in the order of decreasing dielectric constant, but, in view of the possible impurities, their order may not be entirely correct.

§ 2.—It was found that with all the suspensions tried, the liquids in the upper part of the table showed a much greater suspending power than those in the lower part, and that in general, there was a gradual increase in suspending power from the bottom to the top, though there were some reversals in the order. Moreover, the differences in suspending power were very great—a suspension which would settle out perfectly clear within half a minute from any of the liquids, from chloroform down the list, still leaving the liquid turbid for days in acetone and for weeks in water.

No parallelism could be found between the suspending power and either the density or the surface tension, and these will be dismissed from further consideration.

It is also evident that viscosity plays only a minor role, though it has, of course, some influence as, no doubt, the density has also. Comparisons between ether and ether plus naphthalene (moth balls), and between ethyl acetate and ethyl acetate plus naphthalene, showed that the increased viscosity produced by the dissolved naphthalene, did slow down the rate of settling somewhat, but not very much.

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§ 3.—Let us turn, then, to the electrical properties, the specific inductive capacity, and the electrical conductivity. My first idea was based on Coehn's statement that when a liquid and a solid are in contact, the one with the greater dielectric constant becomes positively charged. From this, one would conclude that if the suspension and the liquid had the same dielectric constant, they would be electrically neutral, and would show neither electric migration nor electric osmosis, and that the absence of electric charge on the solid particles, would permit them to stick together at each accidental collision, and so permit rapid flocculation and settling. In the opposite case, of great difference in dielectric constant, we should expect strong migration and osmosis, and great tendency for the solid particles to remain suspended.

The first experiment I made on this point did not give the expected result. Rutile has, for short wave lengths at any rate, a dielectric constant much higher than that of water; it should, therefore, take a positive charge when suspended in water. In fact, however, it migrates in water, as if negatively charged, *i. e.*, against the current. This is perhaps not conclusive, because the dielectric constant for rutile for slow charging is not tabulated, and may be less than that for water. It is evidently the value for slow charging that we must consider here.

Lead carbonate is given as having a dielectric constant of 18.6 for a wave length of 1,200 cm. It should then, if this is any indication of its properties for slow charging, take a positive charge against benzene (D. C. = 2.3). Benzene showed, however, no trace of electric osmosis through a plug of lead carbonate, with a potential gradient of 80 volts/cm., and a very sensitive apparatus; yet quartz and acetone, with about the same difference of dielectric constant, show strong osmosis, the quartz being negative to the acetone.

Quartz, with a dielectric constant about the same as that of chloroform (quartz 4.9, chloroform 5.2), should settle more rapidly from chloroform than from benzene, but no such difference could be observed.

It thus appears that Coehn's statement does not help us much in the present work. Moreover, the suspending power, while approximately parallel with the dielectric constant, shows variations of a totally different order of magnitude. It seems, there-

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fore, unlikely that the value of the dielectric constant is the determining factor, except perhaps indirectly, and we turn to the consideration of the electric conductivity, the only physical property that shows variations at all comparable in magnitude with those of the suspending power.

§ 4.—One thing that makes it a priori probable that the conductivity of the medium is of importance to the rate of settling of suspensions, is that electric osmosis is small or quite absent when the liquid has low conductivity. With a potential gradient of 10 to 17.5 volts per centimeter and a plug of quartz flour in a "U" tube, I could not detect any traces of electric osmosis for benzene ($K < 1.5 \times 10^{-13}$), chloroform ($K = 5$ to 16×10^{-11}), or ether ($K = 5$ to 30×10^{-10}). With ethyl acetate, ($K = 2 \times 10^{-6}$), there was a slight osmosis against the current. With acetone, ($K = 2 \times 10^{-6}$), the osmosis was rapid, as it was also for good distilled water.

Looking again at the table, we see that in a general way, the conductivity of the impure liquids I was using, is nearly parallel with the dielectric constant, or, in other words, the suspending power and the conductivity are in general parallel.

To test this on a given liquid, a comparison was made between benzene ($K < 1.5 \times 10^{-13}$) and benzene plus diphenylamine, ($K = 13 \times 10^{-12}$); the rate of settling was about three times as great in the benzene as in the solution, though the viscosity could not possibly have been changed enough to produce this result. A similar experiment with ether ($K = 3 \times 10^{-9}$), and ether plus picric acid ($K = 2.6 \times 10^{-6}$), showed about the same difference, *i. e.*, a slowing down of the rate of fall to about one-third by the addition of picric acid.

These observed differences of suspending power are by no means so great as the differences observed when we make the same change of conductivity by going from one liquid to an entirely different one. Nevertheless, it seems advisable for the present to look upon the electric conductivity as a prime cause in determining the suspending power of a liquid. Let us now see if we can make up any sort of theory to account for the general run of the observed facts.

§ 5.—It appears that conductivity is necessary for electric migration and for osmosis, *i. e.*, for the suspended particles to

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act as if they had free charges. We also find that where the conductivity is very small, as in all the liquids in the table from chloroform down, the flocculation and settling are very rapid. The simplest view to take, seems to me to be that flocculation and rapid settling are the natural thing which needs no explanation, since they occur in all the liquids which are electrically neutral, so to speak, *i. e.*, those liquids in which the suspensions show no evidence of having electric charges; and that deflocculation or the holding apart of the particles is due to their having electric charges which make them repel one another.

We shall start, then, with the assumption that if no electric forces come into play, the particles of the suspension, which are constantly moving about by reason of the Brownian movements (whatever they may be due to), convection currents, and the different rates of settling of particles of different sizes, are constantly coming into close enough proximity for them to stick together by their own cohesive forces, and, therefore, to form larger aggregates and settle rapidly, as actually happens in the poorly conducting liquids.

We shall then try to form some conception of how the conductivity of the medium may modify this simple state of affairs. In doing this, we shall adopt the language and the ideas of the ionic theory; for, however far it may be from expressing the complete truth, it has enough of truth in it to be useful in the present circumstances. I shall assume, accordingly, that a completely non-conducting liquid is one in which no free ions exist, and that in a highly conducting liquid, many free ions are present. In other words, I shall assume that conductivity and concentration of free ions are in a general way parallel, without, however, making the assumption, which would certainly be erroneous, that the two are strictly proportional.

The question then is: If we start with a given pure liquid and add free ions, how must we expect the suspending power of the liquid to vary with the concentration of the free ions?

§ 6.—In the older theories, before the idea of free ions was familiar, no attempt was made to explain *why* suspended particles should get a contact charge when put in a liquid. Billitzer assumes for colloidal suspensions, which seem to be generally regarded as differing from ordinary suspensions only as regards

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the size of the particles, that each particle acts as an electrode in the sense that it sends ions off into the surrounding liquid, thus remaining with a charge of the opposite sign. It seems rather far-fetched to assume that such substances as quartz, rutile, and hematite send off ions into water, but they all migrate in water as if negatively charged. Quartz and rutile both show electric osmosis with acetone; hematite I have not tried. Quartz also shows slight osmosis with ethly acetate, acting in this case as if positively charged. Rutile and hematite have not been tested with ethyl acetate.

A different interpretation, which has also been given by Patten, seems to me preferable. Instead of assuming that the suspension gets its electrical properties by sending off ions, I shall assume that it gets them by taking up ions, in other words, by selective adsorption of ions, which are already present in the surrounding liquid. It is, in fact, well known that solids, soils in particular, do exert a specific adsorbing or absorbing action on electrolytes, taking out of an aqueous solution of an electrolyte, one ion in preference to the other or others, and thus changing the composition of the solution. Why this adsorption occurs, is a question I shall leave entirely aside; but the fact of selective adsorption seems sufficiently familiar to be an allowable starting point in treating of the less familiar properties of suspensions and suspending liquids. I shall also not attempt to consider the question why most suspensions in water act as if negatively charged, *i. e.*, as if they had taken up the negative rather than the positive ions from the water, nor why water and acetone are positive to quartz, as I have found, while the impure ethyl acetate which I have used, is slightly but certainly negative.

§ 7.—Suppose that a suspension be shaken up in a liquid in which free ions are present. Each particle takes up a certain number of ions, or, if we wish to avoid language which suggests a too mechanic conception of the process, we may say, "a certain amount of one ion." The adsorption is stronger for one kind of ion, usually the negative. The particles, on the whole, become negatively charged. The equivalent ions remaining unadsorbed do not stick close to the particles, for if they did, we should have each particle acting merely as a closed double layer with

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no outside field, or, in other words, no free charge. Hence the equivalent unadsorbed ions are, at any rate, partly free, and the solid particles, having free charges, repel one another. There is thus a deflocculating force, an action opposing the collision, flocculation, and consequent settling out, which are the normal process in a perfectly nonconducting liquid. How will this deflocculating action increase with the concentration of the free ions in the liquid?

Adsorption seems not to be of the nature of a chemical reaction following the law of definite proportions. It is more probably of the nature of the formation of a surface film of solid solution, in which case, the most natural thing to expect would be that the amount of adsorption should be proportional to the concentration of the adsorbed ion in the liquid. Lagergren has shown that the velocity of adsorption is represented by an equation of the same form as monomolecular reactions. Schreiner and Failyer's experiments in this laboratory have also shown that the absorption by soils from percolating solutions is represented by the same form of equation. It seems, therefore, justifiable to assume that the selective adsorption of ions from a liquid by suspended particles, has the same general run as a monomolecular reaction, and that the speed of adsorption and the final amount of adsorption after equilibrium has been reached, depend directly on the first power of the concentration of the free ions in the liquid.

If this is so, and no other modifying causes come in, the average free charge of the suspended particles will be proportional to the concentration of the free ions, or, in general, approximately to the total concentration of the electrolyte, because we are usually dealing with very dilute solutions. Hence we must expect a deflocculating effect proportional to the concentration of the electrolyte, or, in a general way, parallel with the electrical conductivity. The suspending power of a liquid will thus, in general, increase with its conductivity.

§ 8.—But this is not all. It is well known that large concentrations of electrolytes, in water at any rate, not only do not hold up suspensions, but precipitate them. There must therefore be a new action coming in at high concentrations to annihilate or reverse the one already considered, and we must try to find an interpretation of the fact that if the concentration of the electrolyte be high enough, flocculation and precipitation ensue.

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The application of the mass law to the dissociation equilibrium of ions leads to results which are in quantitative agreement with the facts, in a few cases only. But while we cannot say that the predictions of the mass law, as applied to free ions, are verified quantitatively in the majority of cases, taking all sorts of solvents and electrolytes, partly, perhaps, because we do not know how to measure properly the hypothetical concentrations of the ions, it is, nevertheless, safe to use the mass law qualitatively in such general reasoning as the present. We may say, that if in a solution, we have a multivalent negative ion dissociated from a univalent positive ion, the state of equilibrium between the two will be represented by some equation in which the concentration of the univalent ion occurs raised to some power higher than the first. If the neutral body splits into ions, both of which are multivalent, the equilibrium equation will contain the concentration of the ion of smaller valence raised to the higher power.

A suspended solid particle with a single adsorbed univalent ion is, electrically speaking, nothing but a new univalent ion with very large equivalent mass. This is consistent with the phenomena of the electric migration of suspensions. But unless the particles of a suspension are very minute, they will, or may if their adsorbing power is large for any species of ion that happens to be present, adsorb a number of ions. A suspended particle may thus, in general, be regarded as an ion of high valence, generally with a negative charge. Such large ions must finally, like any other ions, come into equilibrium with the electrically equivalent ions of opposite sign, which are, in this case, the unadsorbed ions left partly free in the liquid. Supposing the whole adsorption of the one kind of ion to have taken place, there will follow a certain amount of combination of the other kind of ion, with the solid particle or with the ions on it, until, in the final state of equilibrium, we have on every particle of the suspension, not only free ions of one class, but a certain amount of the neutral undissociated electrolyte also adsorbed. Every such addition of a positive ion to a particle that has previously taken up negative ions, partially neutralizes the electrical charge on the particle, and makes it so much the more likely to come into contact with other particles and to be subject to flocculation and precipitation.

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It seems at first sight as if we had got back to where we started from, and that the electrolyte ought to have no effect one way or the other on flocculation, but here the mass law helps us out. The reaction between the suspended particle, acting in virtue of its adsorbed ions as a multivalent ion, and the non-adsorbed ions of smaller valence, must certainly be expected to be a multimolecular reaction, at least if the reaction is to lead to complete neutralization. This means, according to the mass law, that the speed and the final amount of such neutralization will depend on some power of the concentration higher than the first, possibly much higher. This neutralization, aside from the actual increase of mass of the suspended particles by the adsorption, results only in annihilating the free charges on the particles which we have assumed to be the thing that prevents flocculation. It thus offsets, to some extent, the deflocculating action of the original adsorption, and so tends finally merely to bring the suspending power of the liquid back to its initial value for the pure liquid.

§ 9.—Starting, therefore, with the pure liquid, and adding an electrolyte, as the concentration of free adsorbable ions increases, there is, according to the foregoing considerations:

(1) An increase of the suspending power, *i. e.*, of the time during which the given suspension will stay suspended in the liquid, proportional to the concentration, and

(2) An annihilation of this effect, increasing with some higher power of the concentration and tending finally to reduce it to zero, or to bring the suspending power of the liquid back to its initial value.

It would obviously be a waste of time at present to express these conclusions in the form of equations, but a graphical representation is worth while. In the figure, concentrations are measured to the right from O, and the suspending powers are measured upward. The height of the horizontal line represents the suspending power of the pure liquid. The line A represents the manner in which deflocculation, and therefore suspending power, would increase with the concentration if there were no neutralization. The curve N, falling slowly at first, then more rapidly, and approaching the line A′ asymptotically, shows how the neutralization, or the annihilation of the former effect, increases with the concentration. The ordinates of A′ are equal

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and opposite to those of A. The curve T, with ordinates equal to the algebraic sum of those of A and N, represents the changes in suspending power with increasing concentration, resulting from the simultaneous action of the effects represented separately by the curves of A and N.

The theory, as thus outlined, evidently suggests that as the conductivity of a liquid is increased from zero by the addition of an electrolyte, the suspending power for a given insoluble suspension at first increases, and, after passing through a maximum, decreases toward the value for the pure liquid.

§ 10.—To test this conclusion completely would be a difficult matter. In water, we cannot start with a very low initial conductivity, *i.e.*, we cannot get any real idea of the suspending

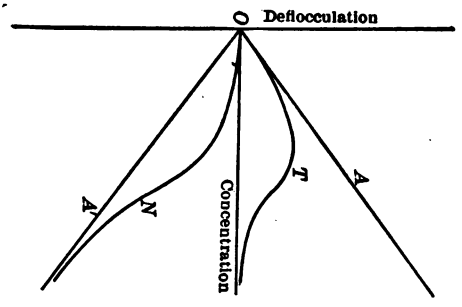

Fig. 1.

power of *pure* water. On the other hand, liquids which, when as pure as they can be obtained, show little or no conductivity, do not readily form solutions which give evidence of the presence of high ion concentrations. Some known facts, however, agree with the prediction of the foregoing argument. It is well known that ammonia and other alkalis have, when sufficiently dilute, a deflocculating action on suspensions of most soils. In other words, increasing concentration of the electrolyte does at first increase, but later decrease the suspending power of the water. The concentration for maximum duration of turbidity is, as might be expected, greater for ammonia than for potassium hydroxide. A similar action has also been observed with oxalic acid.* In both of these cases, the flocculation and settling are much more

* Experiments by J. O. Belz in this laboratory.

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rapid in concentrated solutions than in water alone. This, however, merely means that the lowest suspending power obtainable, while corresponding to concentrations less than those for which the curve T has its maximum, is still far greater than that for *pure* water, which we cannot observe even approximately. Further experiments are, of course, much needed, but there is one other bearing on the point which has not yet been cited.

A series of suspensions of quartz flour was made up, the liquids being benzene, chloroform, ether, ethyl acetate, amylalcohol, acetone, ethylalcohol, water, and aqueous solutions of potassium chloride of the approximate concentrations,

$$\frac{N}{2000}, \quad \frac{N}{1000}, \quad \frac{N}{200}, \quad \frac{N}{50}, \quad \frac{N}{10} \quad \text{and} \quad \frac{N}{1}$$

The suspensions were all shaken up and their behavior observed. In the first four liquids, the settling was rapid, being complete within one minute. The clearing took some hours in amylalcohol, acetone, and ethylalcohol. The $\frac{N}{1}$, $\frac{N}{10}$ and $\frac{N}{50}$ KCL solutions were perfectly clear within a week, but after five weeks, the water and the $\frac{N}{2000}$, $\frac{N}{1000}$ and $\frac{N}{200}$ KCL solutions still show the Tyndall effect in the lower part of the test tubes. The slowest settling has been in the $\frac{N}{200}$ solution, with a conductivity of about 5×10^{-4}, though there is no great difference between this and impure water with a conductivity of 3×10^{-5}. We have here, therefore, another example of the existence of a maximum of deflocculation with less suspending power for both greater and smaller concentrations of the electrolyte. We have, in other words, all through the series of liquids, with all their other varying properties, a general increase of suspending power, with increasing conductivity, to a maximum, and then a decrease.

It looks as though the existence of the maximum might be general for suspensions in aqueous solutions; I have, at any rate, four cases on record that I have seen myself, those namely of NH_3, KOH, KCL, and $(COOH)_2$, a fairly good variety in the electrolytes. It remains to be seen whether the maximum can

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be observed in other liquids than water, as the preliminary increase of suspending power has been, both by varying the conductivity of a given liquid and by comparing different liquids.

The present vagueness of the theory from a quantitative point of view may very likely save it from early destruction. We know, at the start, nothing at all about the relative values of the velocity and the equilibrium constants in the separate adsorption and neutralization reactions, so that we cannot predict *a priori* where the maximum in the curve will be. In may exist for such small concentrations, but be so low as to escape all attempts to detect its existence. Hence we need not be surprised if any given electrolyte has a precipitating effect even at small concentrations. On the other hand, we have left out of account as of minor importance, all questions of density, viscosity, solubility, surface tension, etc., which may, especially when we are considering a series of different liquids, sometimes be of major importance. However, the foregoing considerations are put forth for what they may be worth in suggesting further experiment, and they do not seem to be contradicted by any experimental results that I have compared with them. They might profitably be compared with a great many more known facts about suspensions and colloidal suspensions, but in a preliminary paper such as this, I have not thought it advisable to do so, and have preferred to wait until I have extended my own experiments somewhat farther.

Bureau of Soils, Washington, D. C.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, held at Ithaca, N. Y., May 3, 1906, President Bancroft in the Chair.

THE MIGRATION AND FLOCCULATION OF COLLOIDS, CONSIDERED AS AN ABSORPTION PHENOMENON.

By Harrison E. Patten.

It is well established that the process of flocculation involves a rearrangement of the constituents of the flocculating agent.[1] For example, ferric hydroxychloride[2] when coagulated by sulphates carries more or less of the acid radical into precipitation. In some cases at least, if not generally, this combined (absorbed) acid oxide may be washed out of the precipitate or hydrogel, whereupon the original colloidal solution is reobtained. In the example cited, the hydrogel is lower, of course, in chlorine content, since the chlorine was partly replaced by the sulphate when coagulation took place.

This means that the condition of the ferric hydroxychloride is dependent upon the concentration in sulphate of the water about it. In other words, that there is a distribution coefficient—not

[1] Barus, Am. Jour. Sci., *37*, 122 (1898).
Bodlander, Nach K. Ges. Wiss., Göttingen, 1893, p. 267.
Freundlich, Zeit. phys. Chem., *44*, 136 (1903).
Schulze, Jour. prakt. Chem., *25*, 431 (1882); *27*, 320 (1883).
Hardy, Proc. Roy. Soc., *66*, 111 (1900); Zeit. phys. Chem., *33*, 385 (1901).
Bredig, Anorganische Fermente, 1901, p. 15.
Spring, Bull. Acad. Roy. Belg., 1900, p. 483.
Linder and Picton, Jour. Chem. Soc., *67*, 63 (1895).
Whitney and Ober, Jour. Am. Chem. Soc., *23*, 842 (1901); Zeit. phys. Chem., *33*, 385, (1901).
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W. Biltz and P. Behre, Berichte d. D. Ch. Gs., *38*, 2973 (1905).
Reiss, Betr. Chem. Physol. Path., *7*, 151 (1905).
Daurve, Jour. Chem. Soc. 88, d. 623.
Mathews, Amer. Jour. Physic, *14*, 203 (1905).
Clarke, Bull. No. 167, U. S. Geol. Survey, p. 156 (1900).
van Bemmelen, (See references to his work given below).
Vanino and Hartl, Berichte d. D. chem. Ges., *37*, 3620 (1904).
Hulett and Duschak, Zeit. anorg. Chem., *40*, 196 (1904).
Korte, Jour. Chem. Soc., *87*, 1503 (1905).
Cameron and Hurst, Jour. Amer. Chem. Soc., *26*, 885 (1904).
Cameron and Bell, Bull. No. 30, Bureau of Soils, U. S. Dept. Agriculture (1905).
Cushman, Bull. No. 92, Bureau of Chemistry, U. S. Dept. Agriculture, p. 18 (1905).
Patten, Jour. Am. Chem. Soc., *25*, 186 (1903).
Ostwald, Foundations of Analytical Chemistry, Trans. by McGowan, 1895, p. 26, also Stoechiometrie, 1891, p. 1096; Lehrbuch der allgemeine Chemie, 1891, p. 1093.
Birnbaum and Bomasch, Ding. Poly. Jour., *218*, 148 (1876).
Lieberman, Wien. Akad. Ber., *74*, 331 (1877).
Oechsner de Conick, Compt. rend., *130*, 1627 (1900).
Weffen, Ann. Phys. Chem., *55*, 241 (1845); *59*, 354 (1846).

[2] Linder and Picton, Jour. Chem. Soc., *87*, 1924, 1927 (1905).

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necessarily linear, however—for sulphate between the water and the hydroxychloride. When the proper concentration of the sulphate is reached the hydrogel of iron separates from solution or suspension. Considering the ferric hydroxychloride as a suspension, we can conceive that it acts upon a sulphate solution to split it up into base and acid radical—or it may be, into oxides—by reason of the great surface offered by these minute particles. It is a fact that fine particles of refractory material split salts in solution in this manner.[8]

It is also noteworthy that this splitting action is not a characteristic of what one ordinarily regards as a colloid or gel, since finely powdered crystalloids show the same kind of phenomenon, though less perhaps in degree. Moreover, finely divided crystalloids, such for instance as, rutile, hematite, quartz, etc., remain in suspension indefinitely, are flocculated and deflocculated by the addition of various reagents, migrate under the influence of the electric current, and in general behave in all respects as colloid suspensions.[4]

Why these fine particles remain in suspension is undoubtedly a question as deep-seated as the reason why one element differs from another. The theory of Quincke[5] as rendered quantitative by Helmholtz[6] and developed by Billitzer,[7] Jordis,[8] Hardy,[9] Whetham,[10] Perrin,[11] Whitney and Ober,[12] and Bredig,[13] gives a neat

[8] Way, Jour. Roy. Agr. Soc., *11*, 313 (1850).
J. J. Thomson, Applications of Dynamics to Physics and Chemistry (1888), p. 191.
Oechsner de Conick, Comptes rendus, *130*, 1627 (1900).
Schmidt, Zeit. phys. Chem., *15*, 56 (1894).
van Bemmelen, Jour. prakt. Chem. *23*, 324 (1881); Zeit. phys. Chem., *18*, 331 (1895); Landw. Vers.-Stat., *35*, 72 (1888); Zeit. anorg. Chem., *13*, 233 (1896); *18*, 14, 98 (1898); *23*, 111, 321 (1900); *30*, 265 (1902); *35*, 23, 338, (1904); Arch. Néer. (2) *6*, 607 (1903).

[4] Regarding the evidence of the heterogeneity of colloidal suspensions, and the methods used to estimate the probable magnitude of the colloid particles, consult, G. Bredig, Ann. der Physik, *11*, 218 (1903); J. Tyndall, Heat, *4*, 595 (1894); J. Friedlander, Zeit. f. phys. Chem., *38*, 438 (1901); O. Wiener, Die Erwiederung unserer Sinne, p. 12, Leipzig; F. (Ehren haft) Ann. d. Physik (4) *11*, 514 (1903); J. J. Thomson, Phil. Mag., *38*, 455 (1894).

[5] Uber die Fortführung materialler Theilschen durch stromende Electricität, Ann. Phys. Chem., *113*, 513 (1861).

[6] Studien über elektrische Grenzschichten, Ann. Phys. Chem., *7*, 337.

[7] Billitzer, Zeit. phys. Chem., (1903).

[8] Jordis, Zeit. Elektrochem, *19*, 509 (1904).

[9] Hardy, Proc. Roy. Soc., 66, 95, 110, (1900).

[10] Whetham, Phil. Mag. *48*, 474 (1899).

[11] Perrin, Jour. Chim. Phys., *2*, 601 (1904).

[12] Whitney and Ober, Jour. Am. Chem. Soc., *23*, 842, (1900); Zeit. phys. Chem., *33*, 385 (1901)

[13] Anorganische Fermente, (1901).

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mechanical explanation of electrical endosmose and of the migration of suspended particles, as well as of their flocculation. But as Linder and Picton[14] have shown in their excellent and conservative discussion of this subject, the extant electrical and mechanical theories of colloidal solutions and suspensions are not broad enough to take in all the crucial facts. Further, the idea of Billitzer[15] that in the coagulation of colloids by electrolytes the colloid is always flocculated by the ion of opposite charge, may be developed into the proposition that an ion serves as a nucleus of condensation for so many colloidal particles that the conglomerate is not possessed of a charge. This leads logically to the deduction that the aqueous solution of a colloid is the more permanent the less electrolyte it contains. And, since in the purest water, ions are still conceived as present[16] it follows from this argument that a colloidal solution can have only a limited permanence. Schmauss[17] has developed this idea, but it is at variance with the fact that we have deflocculation produced by exceedingly strong alkali carbonate solutions. And, as may be shown by diaphragm experiments, a coagulated colloid is by no means lacking in a charge of electricity. F. Perrin[18] has found that the charge upon a diaphragm of chromous chloride is positive toward acid solutions, and negative toward basic solutions; and that after contact with the basic solution, the membrane has changed its properties so that a series of washings alternately with acid and alkaline solutions is required to restore the original condition of the diaphragm.

The fact that colloidal suspensions after numerous migrations from one pole to the other and back again, gradually lose most of their "conductivity" and actually part with an acid radicle (Cl, for instance) by diffusion through the gold-beater's skin-diaphragm, does not mean necessarily that the chlorine was originally an ion and carried the colloid with it through the solvent to the skin near the electrode.

It has been shown by Buckingham, in this laboratory that neither the dielectric constant of the medium (sol-

[14] Loc. cit.
[15] Sitzungsber. d. K. d. Wissensch. zu Wien, *118*, 1163 (1904).
[16] Kohlrausch u. A. Heydweiller, Wied. Ann., *54*, 392 (1905).
[17] Ann. d. Phys. *12*, 187 (1903); ibid. *18*, 631 (1905).
[18] Jour. Chim. Phys., *2*, 649 (1904).

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vent) nor the dielectric constant of the solid which is suspended therein are so interrelated as to explain why the particles of the solid remain in suspension. Billitzer[19] has found that Helmholtz's theory of the electrical double layer is inadequate to explain the migration of suspended particles, or their suspension or flocculation. He suggests that the particles of a colloid have their charge modified or partially neutralized, by the charges of the ions they add to themselves, and he considers that the effective charge which causes the particles to migrate is the *excess* of charge remaining from this neutralization.

Franklin and Freudenberger[20] have shown, too, that the platinum will settle out of a colloidal platinum suspension under the action of a centrifuge. But sodium carbonate solution retains fine particles of soil in suspension[21] even after twelve or fifteen hours in a rapid centrifuge; when the suspension is acidfied, flocculation ensues. The reasons then for the settling of a particle or its remaining suspended, are complex. Billitzer's suggestion that an ion serves as nucleus for concentration of particles, and hence their flocculation, is satisfactory to us mainly because we are accustomed to seeing "charged" particles attract each other. This is why the electrical concept of chemical affinity is so satisfying. But there is no deep reason why we cannot use the attraction of gravitation,—whatever that is?—to explain this aggregation as well. Both attractions vary inversely as the second power of the distance. In fact, after all the explanation of the structure of matter based upon the hypothesis of corpuscles and ions, Kelvin has thought it worth while to show that the corpuscles may be held together into atoms by the attraction of gravitation.

E. F. Burton[22] in a most careful research upon colloidal solutions concludes, "The results of these measurements seem to preclude the idea that the charges arise merely from an emission of charged ions from the particles. A co-ordination of the results obtained with different liquid media indicates that the formation of colloidal solutions is due to chemical reaction between the metal and the solvent." And A. A. Noyes[23] expresses a similar

[19] Ann. d. Physik, (4) *11*, 933 (1903).
[20] Trans. Am. Electrochem. Soc., *8*, 29 (1905).
[21] Patten, in this laboratory.
[22] Phil. Mag. [6] *11*, 425 (1906).
[23] Jour. Am. Chem. Soc., *27*, 85 (1905).

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view, "In regard to the cause and character of the electrification, two assumptions deserve consideration; one, that it is simply an example of contact electricity, the colloid particle assuming a charge of one sign and the surrounding water one of the other. This correlates the phenomena of migration with that of electrical endosmose.

It does not, however, give an obvious explanation of the facts that the basic collodial particles become positively charged, and the acidic and neutral ones negatively charged. The other assumption acounts for these facts. According to it, the phenomenon is simply one of ionization. Thus each aggregate of ferric hydroxide molecules may dissociate into one or more ordinary hydroxyl ions and a residual positively-charged colloidal particle, and each aggregate of silicic or stannic acid molecules into one or more hydrogen ions and a residual negatively-charged colloidal particle. To explain the behavior of neutral substances like gold and quartz by this hypothesis, it is necessary to supplement it by the assumption that in these cases it is the water or other electrolyte combined with or absorbed by the colloidal particles which undergoes ionization. It seems not improbable that there may be truth in each of these hypotheses, contact electrification occuring in the case of the coarser suspensions, and ionization in the case of those which approximate more nearly to colloidal solutions."

But none of these considerations suggest an explanation for the flocculation or suspension of fine particles.

Re-solution of a precipitate in excess of the reagent is a common phenomenon. It is generally recognized too, that the precipitate formed from solution is not actually the clean-cut body which we figure in the equation of the reaction which gave the precipitate. Both crystalline and amorphous precipitates show this variation in composition, which may be attributed to absorption exercised by the originally formed precipitate, or in some cases we may consider the precipitate as a solid solution.[24] Tamman[25] also has shown in the case of zeolites that a continuous variation in the crystal angle is obtained with varying quantities

[24] Bancroft, "The Phase Rule," p. 200.

[25] Wied. Ann., *68*, 16 (1897); Zeit. anorg. Chem., *15*, 318 (1897); see also observations on Wellsite by Pratt and Foote, Am. Jour. Sci., (4), *3*, 443 (1897); Zeit. Kryst. Min., *28*, 581 (1897).

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of water in the precipitate; and the investigations of Friedel,[26] Rinne,[27] and others leave no doubt that the same would hold true for other solvents.

It is highly probable that all precipitates are formed first as solutions, pass then to colloidal suspensions, then flocculate and settle.[28] Frankenheim found that ammonium chloride, magnesium chromate, calcium carbonate, and the sulphates of sodium, magnesium, manganese, and aluminum separate in liquid drops when precipitated by alcohol. The passage from amorphous to crystalline condition requires a longer time in some cases than in others, so that frequently we seem to get a crystalline precipitate almost instantaneously. All these statements are of course trite; they are given here to recall that the flocculation of colloidal solutions, or suspensions of finely divided particles by means of acid, basic, or salt solutions is simply a phase of the same general problem.

The work of Tamman on the nature of liquid crystals,[29] and of Hartley,[30] Miers and Isaac,[31] Sonstadt,[32] and T. W. Richards' numerous contributions,[33] all show the great difficulty of forming a clear mechanical conception of the process of crystalization. Quincke's[34] classical researches, too, prove that the process of crystalization is anything but a clean-cut reaction, and that the reverse process, the suspension and ultimate solution of a solid crystalline body, is a gradual reaction not separated into sharply defined stages.

Unquestionably both electrical and gravitational attractions enter to determine the suspension or settling of a particle. What the real nature of these forces, electrical and gravitational, are, we have no notion. Many even would admit, with Professor

[26] Bull. Soc. Min., *19*, 94 (1896).
[27] Jahrb. f. Min., *2*, 28 (1897).
[28] Link, Pogg, Ann., *46*, 258 (1839).
Schmidt, Liebig's Ann., *53*, 171 (1845).
Vogelsang, "Die Crystalliten," Bonn (1875).
Tamman, Ann. der Physik, (4) *19*, 421-25 (1906).
Lehmann, Zeit. f. Kryst., *1*, 97; cf. Patten, Jour. Phys. Chem., *6*, 582-84 (1902).
Bancroft, "The Phase Rule," p. 242.
Ostwald, Lehrbuch, *1*, 1040.
Lehmann, Molekular Physik, *1*, 730, *726*.
[29] Ann. der Physik, (4), *19*, 421-25 (1906).
[30] Proc. Chem. Soc., *22*, 60.
[31] Proc. Chem. Soc., *22*, 9.
[32] J. Chem. Soc. Lond., *89*, 339,
[33] Proc. Am. Phil. Soc., Vol. XI iii, No. *172*, p. 28.
[34] Wiedemann's Annalen, 1902; also, Annalen der Physik, (4) *11*, 486 (1903).

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Babcock, that matter and energy may be complementary manifestations of the same thing. So the picture of a discrete, sharp-angled, polished-faced body floating in a formless medium or solvent, may be far indeed from the truth. And possibly our best generalization of experimental fact will come to be a correlation of the working conditions under which certain bodies can be produced, or certain energies liberated and used. Such for example, is the phase rule, or the current-electromotive force diagram as used in electrolysis, etc.

Whetham's mathematical relation between the coagulating power of ions and the valence of those ions has been found by Linder and Picton[35] not to hold in the case of tetravalent ions, and salts of inorganic tribasic acids. Still there is doubtless some such broad relationship as the one Whetham has formulated. If we recall that valence is a conception introduced to correlate certain physical properties of the elements with their chemical and the electrochemical equivalents, and that the best expression of this relationship is found in Mendelejeff's periodic system, it seems only natural that the power of flocculation should go hand in hand with the valence of the inorganic radical used to induce flocculation. The acid and basic properties of the elements likewise vary with the valence, passing across the table of Mendelejeff from left to right. And even supposing the rule of Whetham ($P. : P_2 : P_3 = X : X^2 : X^3$) to hold, no one would neglect the sign of the charge upon the colloid particle. But positive colloids take to themselves negative radicals, and are then basic; likewise negative colloids take positive radicals and are acid. Consequently flocculation would seem to consist in part, or at least be analogous to, a neutralization of acid by base.

Returning then to purely chemical considerations, it seems that this precipitating action of the negative colloid upon the positive colloid is comparable to the action of (1) a solution of chromic chloride incompletely precipitated by potassium hydroxide upon (2) a solution of chromic chloride which has been precipitated by potassium hydroxide and redissolved in excess of the precipitating agent. In other words, we have a balancing of acid and basic properties, a neutralization, and a consequent

[35] Solutions and pseudo-solutions, l. c. Part IV., pp. 1918 and 1926.

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separation of the chromic hydroxide which is insoluble, in the resulting concentration of KCl.

Now having this neutralization performed, whether the product or compound formed by this neutralization will remain dissolved or suspended in water, brings us back to the original proposition, that we do not yet know why one salt is soluble in water and another is not. Neither do we know why insoluble salts after being formed remain suspended in a high state of fine division, but rapidly aggregate and settle when a slight excess of reagent is added. For example, the precipitation of silver chloride, bromide, and iodide.[36]

In the case of the absorption and migration, and flocculation of various dye stuffs[37] and in the process of dyeing, all of these considerations are applicable. It has been shown that some of the sulphonic acid dyes are split when the process of dyeing takes place and the base with which the sulphonic acid group was in contact remains in solution in the water. This is entirely comparable to the case of the coagulation of ferric hydroxychlorides by sulphates, where the sulphate is found in the hydrogel.

It seems highly probable that the true mechanism of this adsorption and flocculation will be found to involve hydrolysis. By hydrolysis, being meant the general process where a compound separates into two or more parts each of which forms a complete compound, by the addition of one or more constituents of the dissolving or suspending liquids. This extends the process to solvents other than water. It seems likely that a compound is first hydrolyzed, and then being brought into contact with the colloid particles, absorption of a selective nature takes place and the preferred product of hydrolysis is fixed to the colloid, and the other product or products of hydrolysis remain in solution.

Where the body in solution is not subject to hydrolysis, it is absorbed as a whole, since in this case no selective absorption is possible unless the strain upon the compound in solution due to the surface energy of the solid particles is so severe as to decompose the compound.[38]

[36] Quincke, Ann. der Physik, (4) *11*, 486 (1903).
[37] W. Biltz and Paul Belue, Ber. d. D. ch. Ges., *38*, 2973 (1905).
[38] C. F. V. Henri, Zeit. f. phys. Chem., *51*, 19.

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It is very evident that different colloids require a definite amount of adsorbed material to be fixed upon them before they can separate, and when they do separate and the supernatant liquid is poured off and these adsorbed products are washed out with fresh solvent, the process of suspension takes place again,—apparently because there is not enough of the adsorbed material to maintain the colloid in a state of flocculation.

The charge of electricity acquired by these suspended particles of colloid may be compared to the charge of electricity which becomes manifest at the electrodes during electrolysis. In a conductor of the first-class, no decomposition is noticed and no counter electromotive force is observed; but when electrolysis takes place, we have polarity manifested, the decomposed radicals going one to the positive pole, and one to the negative pole; and these electrodes acquire a charge of electricity. There is no experimental evidence to show that in the case of electrolytes, charged bodies exist save at the boundaries. In other words where we have a surge of energy of sufficient strength across a boundary there results a rearrangement of the constituents in that boundary, and as a result of the energy change we have a charge upon the electrode. The surface of a colloidal particle may be thought of as an electrode, which by its absorbing power breaks up the compound in solution, prefers one part of the compound, and therefore acquires a charge of positive or negative sign, depending upon the polarity (acid or base) of the part absorbed. Such an action as this involving the acquirement of a charge of electricity could take place in a solvent of high insulating power or in any other solvent.

The suggestion made above that the products of electrolysis do not separate at the electrodes because they are enabled to give up a charge of electricity, may well be subjected to scrutiny. J. S. Townsend,[39] J. J. Thomson and J. S. Townsend,[40] W. Kosters, [41] and J. Nable, [42] have shown that electrolytic gases still retain an appreciable charge after being conducted away from the electrode chamber in another receptacle. Nernst[43] and Ries-

[39] Phil. Mag. [5] 45, 125 (1898).
[40] Proc. Camb. Phil. Soc. Vol. IX, Pt. V.
[41] Weid. Ann., 69, 1, 12. (1899).
[42] Wiener Anz., 4, (1902).
[43] Ann. der Physik, (Pogg) [iv] 8, 600-624 (1902).

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senfeld[44] also have studied the electrolytic phenomena at the surface of separation of two solvents. And Dr. Horton's research[45] upon the electrical conductivity of metallic oxides, strengthens the view that all electrical conductivity, whether accompanied by electrolysis or not, proceeds by the same mechanism.

It is not necessary to assume the pre-existence of charged ions in the solution, in order that fine particles of colloid, in molar mass, may have a charge upon them. It has been shown that the mere passing of a liquid through fine particles of insoluble matter can generate as high as six volts electromotive force. There is no question that the spreading of fine particles throughout a liquid will cause upon the particles a charge of electricity.[46] Moreover, as stated above, it has been shown experimentally that fine particles can and do split neutral salts apparently merely by reason of the vast extent of their surface. The exact nature of this surface action is unknown, nevertheless it may be considered as a factor.

We have this power of the particles to split neutral salts and thus produce a re-distribution of the energy at the boundary; and this power is added to the surface action of the particle by which it acquires a charge on being suspended in the liquid, even when the liquid contains no electrolyte. Thus we have two sources from which a charge of electricity, upon experimental evidence, may be expected to exist on the surface of these minute particles; and these two sources of charge are totally independent of any assumptions as to previous existence of ions of the salt (or flocculating agent added to the solution) in whose solution the particles are suspended.

The flocculation of negatively charged particles by positively charged colloidal particles is an experimental fact. But it does not follow that this flocculation is a necessary consequence of the neutralization of the positive charge by the negative charge. If this were so, we ought to find a relationship between the dielectric constant of the solvent and the dielectric constant of the suspended material, somewhat similar to the Nernst-Thomson rule.

[44] Zeit. phys. chem., *41*, 346 (1902).
[45] Phil. Mag. [6] *11*, 505 (1906).
[46] Quincke, Ann. d. Ph. u. Ch., *107*, 1, (1859); *110*, 38, (1860).

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The generalization of Perrin,[47] that colloids migrate toward one pole in acid solutions and toward the other pole in alkaline solutions, accords with the view of the interdependence of the migration, absorption and flocculation of colloids.

Consider the colloid globulin.[48] It is an amino acid. With acids it acts as a base; with bases it acts as an acid; with both it yields colloidal solutions. In the case of globulin we can, of course, show the presence of an acid group and of a basic group; and its solution in either acids or bases appears perfectly natural.

Compare with globulin the behavior of zinc hydroxide,[49] aluminum hydroxide,[50] chromic hydroxide.[51] They are precipitated from their salt solution by the addition of alkalies; form colloidal suspensions with quantities of the alkali insufficient for complete precipitation; and redissolved in excess of the alkali, whence they may be re-precipitated, (flocculated), by acids. In many cases the colloidal solutions which are formed short of complete precipitation by the alkali, may be coagulated by the addition of a neutral salt. After the coagulation has taken place, this neutral salt is found to be split; part of it has gone into the precipitate, part has remained in combination with the water.

In the classification of colloids given by Linder and Picton in their Pseudo-Solution, (Part 4, Jour. Chem. Soc., l. c.), ferric hydroxide is classed as a positive colloid, because it is coagulated by neutral salts the acid radical of which is found in the hydrogel; also, because the suspended ferric hydroxide migrates toward the negative pole under the influence of the electric current. In this connection the work of V. J. Hall[52] is interesting. He has shown that ferric hydroxide precipitated in *excess* of potassium hydroxide carries down into precipitation not the acid radical but the base potassium. Thus ferric hydroxide is comparable to globulin, for in excess of alkali it takes the alkali, and in excess of acid, it takes the acid.

We have shown, then, that it is possible to view the migration of suspended particles under the influence of a potential differ-

[47] Jour. Chim. Phys., *2*, (1903).
[48] W. B. Hardy, Jour. Physiol. *33*, 251-337 (1905).
[49] C. E. Linebarger, Jour. Am. Chem. Soc. *17*, 358 (1895).
[50] A. V. E. Young, Am. Chem. Jour. *8*, 23.
[51] Patten, Am. Chem. Jour. *18*, 608.
[52] V. J. Hall, Am. Chem. Jour., *19*, 512.

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ence, as a consequence of selective absorption. This absorption appears to take place in a manner analogous to chemical combination. The acid or basic properties of the radical, taken in connection with those of the undissolved particle, determine whether the radical will be absorbed or not. And the direction of migration will depend upon the sign of the electrical charge which exists upon the particle in consequence of this selective absorption of the solution in which the particle is suspended.

Such a viewpoint is not so satisfactory as a mechanical picture of the process; still A. A. Noyes[53] and E. F. Burton [54] have shown that the mechanical picture is forced to find assistance in a chemical explanation of adsorption and migration. Consequently it may be of value to consider the correlated phenomena apart from any assumption as to the structure of matter, especially as we are dealing with systems which consist of molar masses.

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Washington, D. C.

DISCUSSION.

MR. CARL HERING: I might add that similar migrations of small molar masses can be seen very nicely under the microscope. Under certain conditions which I cannot describe here, you can see the particles of one polarity traveling over the field in one direction and those of the other traveling in the other direction; you can see them bumping into each other, pushing each other aside and coming up to the electrode; but they do not seem to actually touch each other, nor do they seem to actually come in contact with the electrodes; they seem to always remain a certain distance away from each other, and from the electrodes. They remind one of the people moving on a crowded street, some going faster than others and pushing their way through. It is quite an interesting microscopic experiment.

MR. SCHLUEDERBERG: Did I understand Mr. Hering to say

[53] Loc. cit.
[54] Loc. cit.

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you can see these particles with the microscope? Is it possible to see the separate particles plainly?

MR. HERING: Yes, quite distinctly. They are not molecules, of course; they are molar masses.

MR. H. E. PATTEN: Mr. Hering is right, that you can see the particles if they are large enough; but there is also a reason for the question that has been asked. There are, of course, colloidal suspensions or solutions on the border line which are subject to question as to whether they are solutions or suspensions; and our methods of getting at that naturally involve dimensions of the order of magnitude of the wave-length of light. I shall not go into the methods, but we have to strain every point to find out whether those things are really suspensions of discrete particles or whether the particle is a continuous part of the solution; and in the case of quartz particles, Mr. Hering is slightly wrong in his statement there that they don't touch; because in watching the flocculation of a quartz powder put in water, watching the microscope field, it appears very much like the arrangement of the rocks on a railroad track; the particles are distributed at all points, and not aggregated. But when a flocculating agent is added you can see them actually come together; they do touch and stick together. There may be a layer of liquid between them; but as far as you can see they are aggregated.

MR HERING: Of course if the conditions are different, the results may be different. I have no doubt that what Prof. Patten described was the case under those conditions; on the other hand, in the solution which my friend, Dr. Northrup and I happened to examine, we found what I described. The results vary with the conditions of the test. In some of our tests the particles touched each other and agglomerated.

PRESIDENT BANCROFT: There is another side to this. We have here the motion of suspended particles under the influence of applied potential difference. In some experiments we have been making with lead chromate we find that the fine crystals of lead chromate show Brownian movements very well indeed. That of course is a much simpler case than a great many; and it seems to me that we are practically limited there for the source of Brownian movements either to surface tension phenomena or to

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electrical charges (which would probably be the same thing) generated owing to slight changes of equilibrium. Cases of that sort (i. e., Brownian movements with a pure substance, lead chromate or finely divided silica), are really the cases that ought to be studied if we are going to get any satisfactory explanation of the phenomena.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

REPORT ON EXPERIMENTS WITH FUSED SODIUM PEROXIDE ON THE REGENERATION OF AIR FOR SUBMARINES.

By Geo. F. Brindley and Richard von Foregger.

The purpose of these experiments was to prove that a chemical introduced under the name "Oxone," and which is a preparation of fused sodium peroxide, is well adapted to be used for the regeneration and purification of air, especially air that cannot be conveniently renewed by ventilation, and therefore has to be breathed over and over again.

The adaptability of this chemical is clearly manifested by its qualities of liberating oxygen in absorbing moisture, of combining with carbon dioxide, and of disinfecting and deodorizing the atmosphere of the exhalations of living beings. The entire reaction is automatical.

Oxone is a dense body of specific gravity, 2.43 hard, but not brittle, of a grayish color, and capable of being cast into any convenient shape. Thrown into water, it gives off 322 times its volume of pure oxygen gas at 760 mm and 0° C. (From this it will be seen that it can be used for the generation of oxygen, similar to calcium carbide for the generation of acetylene.) Its affinity for water causes it to absorb the moisture of the atmosphere and to give off oxygen. At the same time, a solution of caustic soda is formed, which naturally absorbs any carbon dioxide present. The reaction might be expressed by the following theoretical formulae:

$$Na_2O_2 + H_2O = 2NaOH + O$$

and

$$2NaOH + CO_2 + Aq = Na_2CO_3 + Aq.$$

Having these facts before us, we decided to make a series of experiments on the regeneration of air in enclosed spaces which were to support animal life. We chose the most severe conditions,

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having in view the use of oxone in submarine boats, and we think our results show that we can guarantee to keep nine men alive in a submerged submarine for a period of twelve, as well as forty-eight hours or more, probably within the full radius of action of such a vessel, depending merely on the supply of oxone.

An average man requires 25 litre of oxygen per hour, and as 100 grams oxone furnish 13 litre of oxygen, 192.5 grams would give 25 litre. In other words, one kg. of oxone would sustain a man for five hours and twelve minutes, provided, of course, that he has to breathe the same air over and over again. It will be seen later that these figures agree almost exactly with those we obtain from our experiments.

We took it for granted that if there was sufficient moisture present to decompose a certain quantity of oxone, there would be more than sufficient caustic soda formed to absorb the carbon dioxide.

In our trials we took strong, healthy rabbits averaging in weight seven pounds, and although the weight of a single rabbit was only one-twentieth that of a man, we found that one man exhaled only as much carbon dioxide as ten or twelve rabbits. It is a well-known fact, of course, that many animals exhale 100 per cent. more carbon dioxide than does the average man, weight for weight.

For our experiments we built a strong wooden box, 3 feet x 3 feet x 6 feet long, and tin-lined the same, all seams being carefully soldered. In the top was a plate glass window, which also served as an entrance. This window was so arranged that it could be hermetically sealed by means of luting and kept in place by iron clamps. Inside the box was placed the apparatus, consisting of an electrically-driven blower, so arranged that its discharge was connected to a horizontal sheet-iron cylinder in which was placed the oxone. In addition to this was a cyclometer, an incandescent lamp, wet and dry bulb thermometers, and the necessary food for the rabbits. An Orsat apparatus was placed outside on top of the box, and connected with the inside by means of a glass tube. A wash bottle was also placed on top, and connection made with the inside. The wash bottle enabled us to introduce water if necessary, and the fluctuation of its water level when gas samples were taken, indicated whether the box was air-tight or not.

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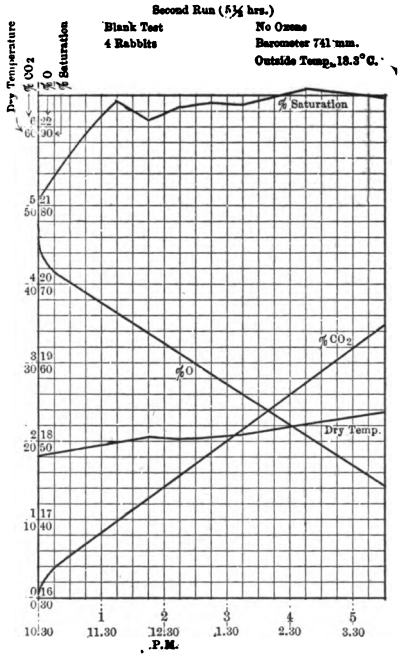
After a preliminary test which indicated things to be avoided than otherwise, we made a blank test on four rabbits, using no oxone. The curves as shown in Fig. 1 are after the first half hour's run, straight lines. In one hour the CO_2 had gone up to 1 per cent., and the oxygen had fallen to 19.7 per cent. At the five and one-half hour reading, one rabbit had collapsed, and we then opened the box.

Our next test was a run with six rabbits in the box and one and

FIG. 1



one-half kg. of oxone placed in a cage of wire netting, arranged concentrically in the sheet-iron cylinder so as to expose as large a surface as possible to the current of air. We noticed that after the lapse of a certain time, all reaction of the oxone ceased, owing, we found, to the formation of a crust of carbonate on the surface of the oxone. The curves in Fig. 2 show that in two hours we arrived at the same condition of affairs shown after one hour in the blank test, and that afterwards the drop was

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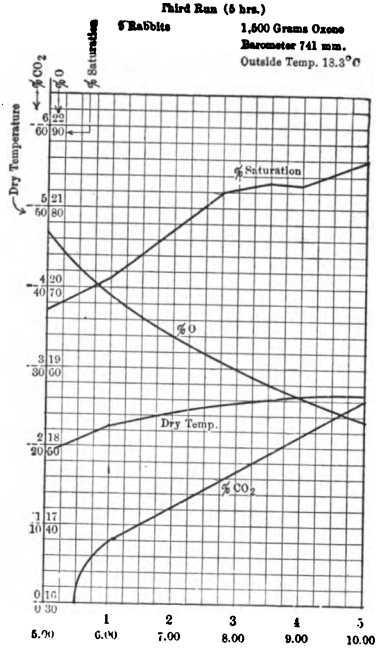
practically steady. That the failure was not due to the want of humidity, was shown by the surplus of the humidity that had accumulated towards the end of the run, on account of not being absorbed by the crust of carbonate.

Among the various means of overcoming the difficulty caused by the formation of the crust of carbonate on the lumps of oxone, we decided upon a mechanical agitator to work the wire netting cage containing the oxone, and so arranged that the rate at which

FIG. 2



the cage was agitated could be regulated. We may at once say that the results were entirely satisfactory, and that the use of this device did not in any way interfere with our original idea, namely, the automatic nature of the process. The use of chemical means to overcome the formation of this crust would have meant an undesirable addition of reagents, an increase in weight, a complication of the process, and perhaps would have endangered the perfectly automatic reaction which we have always kept in mind as the ideal to be reached.

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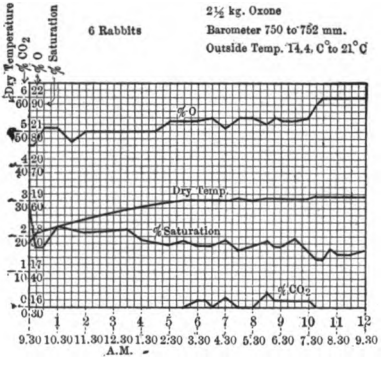
Our first run with the agitating device was a successful one of twelve hours. As before, six rabbits were placed in the box and two and one-half kg. of oxone in the wire cage. It will be noticed on curve Fig. 3 that at the end of the twelve hours, the oxygen was slightly above normal, but steady at 22 per cent., and the CO_2 was down to zero. It should be remarked that one-half of the original oxone remained in the cage at the end of the experiment, so that the run could probably have been extended over fully twenty-four hours, provided the efficiency did not decrease owing to the diminishing surface of oxone in the cage. Later experiments show that this could have easily been done. The slight increase in oxygen in this, as in the following tests, is

FIG. 8

Fourth Run (12 hrs. 5 min.)



accidental, and due to the falling of small pieces of oxone through the wire netting of the cage into the caustic paste accumulated in the outside cylinder, and there acting on the water, generating an excess of oxygen. This defect can, of course, be easily remedied by mechanical means.

The occasional appearance of CO_2 in this run is entirely due to our attempts to determine the slowest rate at which the cage could be agitated. Thus, during the time between 12 a. m. and 3.10 a. m., we agitated the container six times every five minutes. At 3.10 a. m., we agitated only four times in five minutes, and the consequence was the appearance of CO_2. By agitating oftener, the CO_2 could be made to disappear. Finally, beginning at

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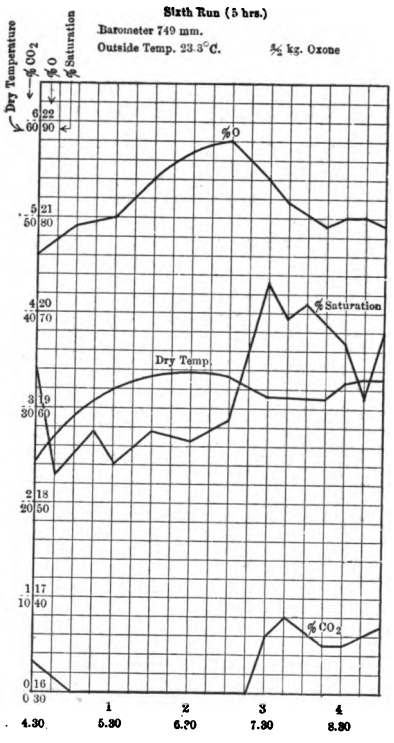
7.30 a. m., we agitated nine times a minute, with the result that CO_2 remained at zero and the oxygen steady at 22 per cent. The humidity after jumping down from 58.6 per cent. to 46.5 per cent. saturation, at the start gained slightly, and then remained almost constant at an average of 48 per cent. The slight drop in percentage towards the end is what one would expect from the

FIG. 4.



rising temperature. The absolute humidity is steady at an average of fifteen grams per cubic meter of air. We would call particular attention to the fact that on opening the box at the end of the run, not the slightest odor from the rabbits could be detected, and that the animals themselves were in good condition.

We would also point out that, inasmuch as only one-half of the oxone had been consumed by the end of this run, the curves

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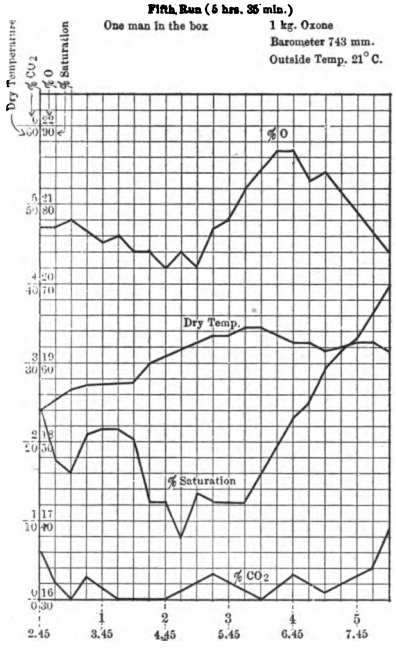
shown do not indicate what would take place at the end of a run where all the oxone had been used up.

In our next experiment, therefore, we started with a comparatively small amount of oxone and ran until it was all exhausted. The results obtained are shown in Fig. 4, which furnished an interesting, but not smooth, curve. To determine the efficiency of this process, the amount of oxone remaining in the cage when the oxygen begins to drop should be noted. We started with only

FIG. 5



500 grams in the cage, and to see what influence artificially-produced humidity would have, we put 100 cc. of water in the bottom of the cylinder surrounding the oxone cage. The introduction of this water proved a disadvantage, owing to small pieces of oxone from the cage dropping into it and there generating excessive oxygen. At seven o'clock the oxygen was up to 21.8 per cent., although very little oxone was left in the cage. At 7.15 we stopped agitating altogether, with the result of an

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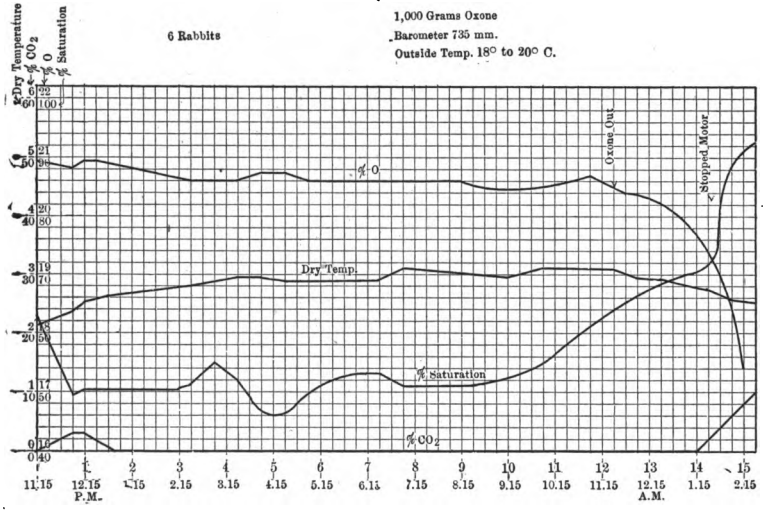
immediate drop in oxygen and rise in CO_2. At 7.30 we started agitating the cage again, and although a partial recovery towards normal conditions was shown, the amount of oxone left was too small to bring about a complete restoration. At 8.00 o'clock all oxone was used up, and one hour later we shut down; the air inside showed oxygen 20.9 per cent., and CO_2 0.7 per cent. It is interesting to note the considerable increase in the humidity and the drop in temperature the moment we stopped agitating the cage.

FIG. 6

Seventh Run (15 hrs. 15 min.)



Slight variations in the temperature readings, and also in the humidity curve, were caused by the heat radiated from the electric lamp used for taking thermometer readings, etc.

Again, on opening the box, no trace of odor could be detected.

This test proved conclusively that the process works with 100 per cent. efficiency, or perhaps more, when one stops to consider that with a properly constructed apparatus, CO_2 will continue to be absorbed by the caustic liquor in the outer cylinder for some time after the oxone has disappeared—there will then, of course, be no oxidation of the toxic contents of the air.

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In order to test more thoroughly the flexibility of the process and to make closer observations inside the sealed box, one of us undertook to play the role of the rabbits in previous runs. Curve sheet No. 5 shows a run of nearly six hours with a man sealed up in the box, with one kilogram of oxone in the cage.

This test, like our previous ones, was not made with the object of getting smooth curves, but rather to show any unevenness under extreme conditions. In fact, the whole test is extreme, when one considers that the man was sealed up in a space not over four times the size his coffin would be. One of the interesting features of this test was the smoking of cigarettes by the man inside. The various points where the CO_2 curve goes up from zero to 0.2 and 0.3 per cent., shows the times the cigarettes were smoked. Another most noticeable thing was the absorption of the smoke and the drop of CO_2 to zero again within fifteen minutes after the extinction of the cigarette. Also when the box was opened, there was not the faintest smell of cigarette smoke.

The marked increase in humidity is in all probability due to the fact that for a few moments a wet towel was held in front of the fan inlet and 50 cc. of water placed in the bottom of the outside cylinder during the third hour's run. The presence of this water on the bottom of the outer cylinder was again a disadvantage, owing to small pieces of oxone falling into it and producing an increase in oxygen.

After four and one-half hours, nearly all the oxone had gone, only a few small pieces remaining in the cage, and the oxygen started to go down.

How quickly the air becomes vitiated in such confined spaces, is shown by the fact that during the short time it took to get the man sealed up and the motor started, 0.6 per cent. CO_2 had accumulated in the box. It will be noted, however, that within thirty minutes this was completely absorbed.

Time and space will not admit of our going into all details marked on our test sheets by the experimentor, inside and outside the box. It is essential to note, however, that the man inside asserted that throughout the run he felt exceedingly well, in fact, better than before he entered. He described the conditions as being similar to a hot, dry summer's day, and only towards the end were the effects of increasing CO_2 and humidity noticeable.

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In the following tests, which represent the last of the series, we made use of the experience gained in previous runs, and obtained curves of more ideal shape. We also paid special attention to determining the amount of oxone necessary per unit per hour, when running under economic conditions. The same set of six rabbits was used, as in previous runs, as they were all still strong and healthy. Five and one-half cylindrical cakes of oxone, weighing one kilogram, were placed in the cage. No water was placed in the outside cylinder, so that all humidity which acted on the oxone came from the animals themselves. During the entire run, the cage was agitated from fifteen to twenty times per minute, and special pains were taken to avoid any heat being radiated from the electric lamp to the instruments.

The result of this test is shown by the regular curves obtained, Fig. 5. There is an irregularity at the fourth and fifth hours in the humidity curve, which was due to our turning on the electric light in the box to please visitors. The increase of humidity at the eleventh hour is due to the small amount of oxone remaining. After twelve hours and fifteen minutes, all oxone had disappeared, and the oxygen commenced to go down gradually. It will be noticed, however, that the CO_2 continued to be absorbed by the paste in the outer cylinder for two hours after all oxone had disappeared. At the fourteenth hour, CO_2 appeared, and in order to add a blank test to the experiment, the fan and agitator were stopped. The effect is illustrated by the inclining curves, an interesting feature of which is the rapid increase in humidity to a point not far from saturation.

From these results we are correct in saying that one kilo of oxone is sufficient to regenerate 54 cubic feet of air in an enclosed space in which are confined six rabbits for thirteen hours. Our observations also show that six rabbits will vitiate the air at one-half the rate a man would. In other words, one-half kilo of oxone will support six rabbits the same time that one kilo would support one man, which naturally corresponds with our experimental figures.

It will be interesting to apply these results to the practical example of a submarine boat.

The box used in our experiments had a capacity of 54 cubic feet, or 1,512 litres of air, while that of a submarine has on an average, 2,700 cubic feet, or 75,600 litres.

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Placing the limit of CO_2 at 0.9 per cent., which was obtained after five and one-half hours in run five as a basis to figure on, we find that this corresponds to 13.6 litres CO_2 in the box. A man excretes about 0.315 litres of CO_2 per minute under ordinary conditions, so that the air in our box would last him forty-three minutes, twelve seconds, before the amount of CO_2 reached 0.9 per cent. In a submarine of 75,600 litres air space, 0.9 per cent. would mean 680.5 litres CO_2. If nine men are to stay in that space, each of them exhaling 0.315 litres CO_2 per minute, it would last four hours before the 0.9 per cent. mark was reached, no oxone being present. If each man was supported by one kilo of oxone, or nine kilo in all, it would be ten and one-half hours before 0.9 per cent. CO_2 was reached. This limit of 0.9 per cent. CO_2 is, of course, too high for practical purposes; but we are safe in saying, from the result obtained, that they would be perfectly safe for fully nine hours, and that with eighteen kilo, or forty pounds of oxone, they would be safe for at least fourteen hours. So that if forty pounds of oxone would supply nine men in a submarine for fourteen hours, one man would require 0.317 pounds per hour, or practically one-third of a pound.

To sum up, then, we may say that in our opinion the described experiments form a good basis on which the regeneration of air may be worked out. Also, that the process used is based upon (1) the generation of oxygen; (2) the absorption of carbon dioxide; and (3) the elimination of the toxic parts of excreted air, apparently by an oxidation taking place between the vitiated air and the oxone while in a state of reaction.

It is evident that the application of this process to submarines, although very important, forms only one of its many uses. To enlarge upon the variety of uses this process could be put to would take far too much time. We are satisfied to have simply brought before you the fact that henceforth it will only be a question of oxone supply to support the life of nine men in a submarine for any length of time.

We cannot close this paper without expressing our indebtedness to Mr. F. A. J. FitzGerald, of Niagara Falls, for the very valuable suggestions and assistance he gave us in the above experiments.

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DISCUSSION.

MR. A. E. ASHCROFT: I think this paper is an extremely interesting one; and the subject is one which may come to be an extremely important one; because the regeneration of air in closed spaces has an almost infinite number of possible applications. If it can really be done completely, it is exceedingly important.

There is just one point about this that the authors have not quite gone into; and I would like to have some of your physiological chemists at this university enlighten us on the subject. The question that occurs to me is this; when air is taken into the lungs it can either oxidize carbon to CO_2, in which two atoms of carbon would be rejected to one of oxygen taken in and one molecule of carbonic acid would have to be absorbed, therefore you would not have a cyclic regeneration; or the other method in which the chemistry of the lungs might act, could be that it would oxidize CO to CO_2 so that there was only one atom of carbon rejected and two atoms of oxygen taken in; in which case you would have a perfectly cyclic process. Can any one please tell me what is the chemistry of the lungs?

MR. S. S. SADTLER: I think he absolutely demonstrates the cyclic character of this process so far as I can see; because the curves are affected the very moment there is a lack of oxone; and as long as there is oxone, there is almost a perfectly straight line. The curves practically show the absence of CO_2 and the moisture kept down when the oxone was present and the immediate running up of CO_2 and moisture when the oxone became exhausted.

MR. ASHCROFT: I don't think you caught my point. It is a point which I feel sure can be answered and cleared up by any one up in the subject of physiological chemistry, which I am not and I notice very few here seem to be. The point is, whether in breathing you take in more oxygen than you eject CO_2, or an exactly equivalent amount. I think it must be thoroughly well known by physiological chemists what happens in the lungs.

PROF. DENNIS: Might I ask a question on chemistry? The report stated that the moisture of the air decomposed the sodium peroxide. Will that take place simply in the presence of water?

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MR. SADTLER: Yes, because in his generator he has water, which acts upon the peroxide and gives the caustic soda and the oxygen required.

PROF. DENNIS: Has it been demonstrated by a gas analysis, that in a closed space in the presence of atmospheric moisture, sodium peroxide will gradually increase the oxygen? I had supposed that oxygen would not be continually given out by mere action of peroxide on a weak acid.

MR. SADTLER: I believe it gives it off as long as the water is in contact with it.

PRESIDENT BANCROFT: I can answer that from a certain standpoint by quoting Mr. von Foregger at the Bethlehem meeting. He said there that there is a radical difference in the behavior between the sodium peroxide that we have in the laboratory and this sodium peroxide which we have on the market which has been fused; and that it is not safe to reason at all from one to the other. He did not explain exactly why having fused it should make it much more energetic than before.

MR. SADTLER: I believe there is a catalytic agent there that helps the oxygen; but Dr. von Foregger said that that was not necessary; but to me it seemed that he explained the action as largely that of the condensation of the peroxide and that the heat generated in that confined space, eliminated the oxygen of it more freely than it would with hydrogen peroxide, which was loose and open and the heat of reaction was not so concentrated. That was the impression I got from what he said.

MR. CARRIER: I have had considerable sodium peroxide formed undesirably in my experimental work. It is very impure and it is in a very finely powdered form; and when you put that into water the action is so violent that it forms steam instantly as it touches the water; it would seem that a catalytic agent is absolutely essential. I do not believe they put it in there for the fun of it.

PRESIDENT BANCROFT: That certainly seems a more probable explanation than the one given before—that the thing in a condensed form reacted more rapidly because it had been fused and therefore contained the heat necessary to fuse it.

PROF. DENNIS: Of course, the university fails in its function if it cannot furnish us information on any topic; so I have called

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upon the Department of Experimental Physiology for an answer to our questions. Prof. Kingsbury tells us that, approximately, in our normal diet the volume of oxygen inhaled will equal the volume of carbon dioxide exhaled. The ratio is about 10 to 9; very close to 1 to 1. Is it moist in this submarine all the time?

MR. SADTLER: That referred to the moisture of the products exhaled from the bodies.

PROF. DENNIS: Then the atmosphere of the closed chamber is dry?

MR. SADTLER: Dry, otherwise than from the animals that are in it, as from the moisture of the breath or by perspiration.

PROF. DENNIS: Is this the only moisture that is there?

MR. SADTLER: Yes.

PROF. DENNIS: Of course, we have no means of knowing.

MR. SADTLER: Excuse me! I believe they did introduce water in one experiment; and if I remember rightly that did not have very much influence on it.

DR. E. F. ROEBER: I think they always generated the gas with the aid of water.

PRESIDENT BANCROFT: If necessary I suppose it would be possible to build some sort of a submarine with an explosive safety valve.

MR. HENRY HOWARD: As this question has been brought up again I might say that sodium peroxide is a very convenient source of oxygen, and I made use of that fact once to save a man's life who had been rendered unconscious by gas. We did not happen to have any tube of oxygen in our works at the time of the accident, but remembering that we had a can of sodium peroxide I used it in an ordinary hydrogen generator with water, bubbling the gas through a single wash bottle and forcing it into the man's lungs through a rubber tube placed in his mouth by the aid of artificial respiration. Before the oxygen was administered the man had stopped breathing and his heart had stopped beating; while inside of fifteen minutes after I started to give him oxygen he had regained consciousness.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

ALTERNATING CURRENT ELECTROLYSIS WITH CADMIUM ELECTRODES.

By G. R. White.

When an alternating current is passed through a solution of sodium hyposulphite with cadmium electrodes, a precipitate of cadmium sulphide is formed. This problem has been studied by Richards and Roepper, who have taken out a patent covering this phenomenon as a process for the manufacture of "cadmium yellow." LeBlanc and Schick[1] have also published a paper, "Electrolyse mit Wechelstrom," in which they give efficiencies obtained with various frequencies from 0 to 17,600 per minute. Examination of their results show that the efficiency, or as they put it, "electrode loss in o/o" drops off materially as the frequency increases, and at the higher frequencies (9,600 and 17,600 per minute) to nothing. The efficiency found by them with a frequency of 6,900 per minute is 0.6 o/o. It is the purpose of this paper to show that this efficiency can be very much increased. The current used in this work was an alternating current used for lighting and was sixty cycles or 7,200 alterations per minute. The results obtained by LeBlanc and Schick at 6,900 alternations was chosen for comparison with the results obtained in this case at 7,200 alternations. The efficiencies obtained varied from 0.81 % to 35.88 %, under conditions which will be stated later.

The following variables were studied:

1.—Current strength.

2.—Temperature.

The electrodes were made from cadmium rods which were first hammered down to such a thickness that they could be easily rolled, and were then rolled out to a thickness of about 2 mm. Six electrodes were made from rods in this manner. The usual procedure was to run two electrolytic cells in series. In each cell,

[1] Zeit. phys. Chemie. *46*, 213 (1903).

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three electrodes were placed, the two electrodes joined together in one beaker being connected with the single electrode in the other. As a rule, one electrolytic cell was kept at one temperature and the other at a different temperature. The temperature difference was usually a 20° interval— 101° and 80°, 60° and 40°, 20° and 0°. No especial care was taken to keep the temperature exactly at the points mentioned above, but the average temperature for an hour's run was very close to these values. The electrolyte was a 20 % solution of commercial sodium thiosulphate. In order to keep the concentration constant, especially in the cells, at 101°, water was added from time to time.

The reason for using three electrodes was that at first it was decided to record the current densities, and the entire surface of the electrode in the center was to be used as the basis for the calculation. Later it was found that the current density was of minor importance, but the three electrodes were kept because the electrode loss was thus divided among three electrodes instead of between two, thus preventing, in a measure, the too rapid corrosion of one electrode, and consequent liability to scaling off.

When the current is passed through the electrolyte, the electrodes at first become coated with a brown oxide film, and hydrogen is given off. Then the sulphide begins to form, but not at once, for it is soluble in the sodium thiosulphate. The electrolysis was carried on for an hour; the current and temperature was kept fairly constant, readings being taken every five minutes and the average taken. The average current for a run was then multiplied by $0.5,807 \times 3,600 - 0.5,807$, being the electrochemical equivalent of cadmium in milligrams per ampere second, and 3,600 the number of seconds in an hour. This was taken as 100 o/o, and the efficiencies are all worked on this basis. Three current strengths were used, approximately 3, 2 and 1 amperes. The electrode surface of the electrode in the center was 15 square cm.

It was found that the efficiencies for the temperature differences of 101° and 80° were uniformly greater for 101° than for 80° with all current densities, as the following results will show:

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TABLE I.

Current (Average.)	Loss in Grams.		Per Cent. Efficiency.	
	80°	101°	80°	101°
2.98	0 3268	0 8784	5 58	14.09
2.94	0.6758	1.1732	10.99	19.08
3.10	0.3676	0.5792	5.67	8.94
1.87	0.1546	0.3940	3.95	10.07
1.87	0.1984	0.4438	5.06	11.35
1.96	0.0762	0.4052	1.86	9.88
0.98	0.0850	0.2298	4.19	11.21
0.85	0.0766	0.2340	4.30	13.15

Examination of the above data shows that, while the percentage efficiency varies within wide limits, the loss is greater at 101° than at 80°. This might be explained by the fact that at 101° the solution is boiling quietly and the movement of the electrolyte keeps the electrode surface free from the sulphide, so that new material is constantly exposed to the action of the thiosulphate. From the consideration, it was thought that the efficiency at 101° might be raised still higher by stirring, so one of the electrodes was rotated, but the efficiency under these conditions was not affected in the slightest.

It was noted that the current density had but little effect on the efficiency, so in most of the following runs, a current of about 3 amperes was used, because that reading could be obtained most readily and most accurately on the ammeter which was used.

The two temperatures next tried were 40° and 60°. The following are the results:

TABLE II.

Current (Average)	Loss in Grams.		Per Cent. Efficiency.	
	40°	60°	40°	60°
3 0	0.1370	0.2380	2.18	3.79
2.96	0.2232	0.2742	3.44	4.43
2.92	0.1436	0.1916	2.35	3.14

Here again it is seen that the current efficiency is higher at

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the higher temperature and that the difference is less marked than between 80° and 101°.

Then some runs were made at 20°, and a very striking fact was noted. There were two runs at this temperature. Two electrolytic cells were run in series, and these are the results:

TABLE III.

Current (Average)	Loss in Grams.		Per Cent. Efficiency.	
	20° (in Series) 20°		20°	20°
2.90	0.3656	0.2796	6.03	4.61
2.92	0.2832	0.1706	4.64	2.79

It will be seen that the efficiency was higher here than at 40° and 60°. What is the explanation for this? It is a well-known fact that the ease with which an electrode dissolves depends largely, if not entirely, on the condition of the electrode surface. It is very probable that this high efficiency is due to the fact that the electrode, by constantly dissolving away, has exposed a layer of metal, which was acted on much more readily than the metal previously exposed. As a check then to see if the efficiency would be greater than the efficiency obtained in the previous run, the electrodes were run at 101°, with a current of 1.85 amperes. This current was used instead of three, because with the larger current, so much precipitate is formed that "bumping" occurs. The results lend weight to the assumption that a more readily soluble layer of metal was found, because a much higher efficiency is noted.

Current (Average)	Loss in Grams.		Per Cent. Efficiency.	
	101° (in Series) 101°		101°	101°
1.85	0.6708	0.4378	17.15	11.19

For sake of comparison, the efficiencies at 20° and 101° are given below. The electrodes which gave efficiencies of 6.03 per cent. and 4.64 per cent. at 20°, gave 17.15 per cent. at 101°. Further, the electrodes which gave efficiencies of 4.61 per cent. and 2.79 per cent., gave 11.19 per cent. at 101°. The highest efficiencies given by these electrodes before was 9.88 per cent. and 5.67 per cent. respectively. Here it is seen that the efficiency is very much higher. It is therefore reasonable to conclude that

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this increased efficiency at 20° is due to a layer of metal which dissolved very readily.

Some runs were then obtained at 0° and 20°. The zero, of course, is only approximate, as it is very difficult to maintain the temperature at this point with a current of nearly three amperes. Again the results are very striking—showing a greater efficiency at zero than at 20°.

TABLE IV.

Current (Average)	Loss in Grams.		Per Cent. Efficiency.	
	20°	0°	20°	0°
2.91	0.0492	0.2836	0.81	4.67
2.89	0.1698	0.3706	2.82	6.13

In the second set of figures, the electrodes were reversed, that is, the electrodes which at 20° gave an efficiency of 0.81 per cent., at 0° gave 6.13 per cent. It might seem that this was very good evidence that the efficiency was higher at 0° than at 20°. The conclusion does not seem logical, for no good explanation can be offered for this increase in efficiency at 0°. Examination of the loss of weight of the individual electrode will throw some light on this question. For comparison, the six electrodes were also run at 0°, with a current of 2.85 amperes. The losses are here tabulated:

TABLE V.

Current	A	B	C	D	E	F
2.91	0.0164	0.0158	0.0170	0.0556	0.0650	0.1630
2.89	0.0650	0.0576	0.2480	0.0112	0.0192	0.1394
2.85	0.0464	0.0460	0.1360	0.0102	0.0178	0.1452

The underscored figures show the loss of the electrodes which were in the solution at 20°. The electrodes C and F were the electrodes in the center of the group of three in the cell. The figures from left to right show the loss of each electrode when the six were run in series. Examination of these figures will show very clearly that the temperature is a minor factor, and that the loss depends on the nature of the electrode surface. It will be

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especially noted that the loss of the electrodes under very nearly the same conditions varies within extremely wide limits. It seems that, if the loss were a function of the temperature only, it should not fluctuate at the same temperature, but should be a fairly constant value.

The statement that the electrode loss depends almost entirely on the condition of the electrode surface is best seen by a tabulation of the losses of each electrode under the various conditions:

TABLE VI.

No.	Current.	Temp.	Electrode Loss in Grams.		
			A	B	C*
1	1.96	101°	0.0280	0.2242	0.1530
2	1.85	101	0.1510	0.1524	0.3674
3	3.10	80	0.0796	0.0930	0.1950
4	3.00	40	0.0124	0.0124	0.1122
5	2.96	40	0.0314	0 0336	0.1582
6	2.92	60	0.0360	0.0570	0.0986
7	2.90	20	0.0432	0.1118	0.2116
8	2.92	20	0.0178	0.0170	0.2484
9	2.91	20	0.0164	0.0158	0.0170
10	2.89	0	0.0650	0.0576	0.2480
11	2.85	0	0.0464	0.0460	0.1360

* C is the electrode in the center.

The next group of figures gives the losses of the other three electrodes, and are numbered in the same order as those above, indicating that they were run in series.

TABLE VII.

No.	Current.	Temp.	Electrode Loss in Grams.		
			D	E	F*
1	1.96	80°	0.0214	0.0216	0.0332
2	1.85	101	0.1404	0.0972	0.2002
3	3.10	101	0.2480	0.1354	0.1958
4	3.00	60	0.0584	0.0526	0.1270
5	2.96	60	0.0224	0.0314	0.2204
6	2.92	40	0.0202	0.0132	0.1102
7	2 90	20	0 0388	0.0472	0 1936
8	2 92	20	0.0180	0.0304	0.1220
9	2.91	0	0.0556	0.0650	0.1630
10	2.89	0	0.0112	0.0192	0.1394
11	2.85	0	0.0102	0.0178	0.1452

* F is the electrode in the center.

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Examination of these figures will show that there is absolutely no regularity in the amount of metal lost. The loss varies widely at the same temperature and with approximately the same current.

It was thought that if the condition of the electrode surface could be made more uniform, the rate of solution would be very nearly equal. Some electrodes were therefore cast from cadmium rods—two were chill cast in graphite moulds, and two others, also chill cast, were annealed for a week at the temperature of boiling napthalene (217°). These electrodes were then run in the usual electrolyte with a current of 2.21 amperes, and again with 2.50 amperes. It was found that the electrodes which were annealed dissolved very evenly, as far as weight was concerned. Furthermore, a larger quantity of metal dissolved from the annealed than from the cast. The cast electrodes, moreover, lost widely different amounts, indicating lack of uniformity. The results are given here:

TABLE VIII.

Current.		Loss in Grams.				Per Cent. Efficiency.	
		Annealed.		Cast.		Annealed.	Cast.
		1	2	1	2		
I	2.21	0.6202	0.6186	0.3236	0.5092	26.81	18.03
II	2.50	0.9116	0.9000	0.8952	0.9812	34.64	35.88

These results indicate that even under conditions where the electrode surface was supposedly uniform, the quantity dissolved may vary widely. The column marked "annealed" shows this very markedly in runs I and II. It will be noticed, however, that the quantities dissolved in each run are very uniform. The column marked "cast" shows marked fluctuation, but fluctuation is in the same direction. The efficiencies vary widely, and indicate very plainly that in this case the metal towards the center of the electrode corrodes much more rapidly than the metal at the surface.

In all cases it is noticed that the upper part of the electrode is most attacked. Here polarization is prevented because of the oxygen from the air dissolving in the electrolyte. The electrodes dissolve very unevenly. Sometimes the metal will be dissolved

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out down the middle of the electrode. Again, the solution may take place in one or two places, where deep depressions will be formed. The solution is always more pronounced at or near the surface. In fact, in one run so much of the electrode dissolved at the surface, that the electrode was cut through and the lower part fell to the bottom of the beaker. The annealed electrodes, the surface of which might be assumed to be fairly regular, showed a very marked irregularity of solution, while the chill cast electrodes dissolved very regularly, except at the surface of the electrolyte, where the solution was very marked.

At the completion of a run, the sulphide adhering to the electrode is washed off with water, then rinsed with alcohol, and allowed to dry before weighing. The electrodes are always covered with a coating of brown oxide.

The results of the work in summary:

1.—The efficiency is too low for a commercial process. The precipitate, moreover, is apt to be polluted with bits of the brown oxide film, which would be objectionable in a commercial product and render special treatment for its removal necessary.

2.—The efficiency as shown by LeBlanc and Schick is much too low.

3.—The efficiency is practically independent of the current strength.

4.—The efficiency is also practically independent of the temperature and of stirring.

5.—The efficiency depends almost entirely on the electrode surface.

The work was suggested by Professor Bancroft and carried out under his direction.

Cornell University.

DISCUSSION.

PROF. W. LASH MILLER: The two electrodes that were revolved are different from the others; they are deeply corroded just where they came out of the liquid. Is that due to action of the air?

MR. WHITE: I think it is. We noticed that in every case the

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electrode was dissolved more at the surface of the electrolyte. We accounted for it by the fact that polarization was prevented at this point by the oxygen of the air. In one case we were running a rather thin electrode and we found that the electrode was corroded completely through at the surface of the electrolyte and the electro-deposition of metallic sodium from an aqueous solution run at this point.

MR. PATTEN: While that statement of Mr. White's may be true in this case, I would like to suggest that entirely apart from conditions that involve oxygen or any constituent of the air, when you dissolve a rod in a liquid you get a circle of deep corrosion about the rod right at the surface of the liquid.

PRESIDENT BANCROFT: May I interrupt you, to say that that is true, I think, only in case you do not stir the solution? Spring made some experiments to show the remarkable solvent action of a surface, and afterwards he withdrew those experiments. The phenomenon took place only when the solution was not stirred. There was a steady current set up due to a denser liquid forming and corrosion took place more readily at the surface because fresh solvent was brought in there and not due to the fact that it was a surface. I think that explanation would not hold in this particular case.

MR. PATTEN: I hardly thought it was an explanation.

DR. J. W. RICHARDS: I felt very greatly interested yesterday in seeing this experiment performed in the laboratory. It recalled to me the first meeting of our society, where I tried to show the same thing and it would not work, although I had worked it myself in my own laboratory. The reason is given in the early part of the paper, where it says that when the sulphide begins to form, the cadmium sulphide doesn't precipitate at once, as it is somewhat soluble in the sodium thiosulphate. After the electrolysis is carried on an hour you get a good precipitate. It takes some time to get the operation going well and that time was not available at the first meeting where I tried to show it; the consequence was that the precipitate did not come down when it was wanted. At that time we did not know as much about the conditions of forming the precipitate as we do now. One quite interesting fact is shown in this paper, where the efficiency (as I read it) has gone up to 34 per cent. with an annealed elec-

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trode, being greater for a current of 2.50 amperes than for a current of 2.21 amperes. It seems as if the efficiency there was larger with the larger current and had reached nearly 33 per cent., which was higher than I myself had ever expected to obtain from an alternating current electrolysis.

PRESIDENT BANCROFT: It is not safe to draw any conclusion as to effect of current density or concentration or temperature from any single set of experiments. I have no doubt that all those factors affect the yield to a certain extent; but as that variation is probably very small it disappears absolutely in comparison with fluctations from fifteen to twenty-five per cent., or even more, depending on minor changes in the electrodes which you cannot represent quantitatively. Until some one can devise a method for making an absolutely reproducible electrode, the changes in efficiency due to the other factors have simply to be classed under the head of not being measurable.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

ELECTROLYTIC CHROMIUM.

By M. Le Blanc.

Last year there appeared two articles on "Electrolytic Chromium," by Carveth and Mott, and by Carveth and Curry,[1] in which reference was made to my monograph on "The Preparation of Chromium and Its Compounds with the Aid of the Electric Current." At the close of the last article, the statement appeared: "The criticisms of Le Blanc on the work of Geuther, Placet and Bonnet, and Street, need radical change. The only justification for such criticism was due to the experimental conditions not having been described in sufficient detail by the various workers."

As, by reason of this remark, every reader must come to the conclusion that my criticism was entirely wrong and unjustifiable, I am forced to put the matter in the proper light. The name of Geuther appears in my monograph, in fact only, in the following sentence: "He (Buff) was led to this experiment by a statement of Geuther's, who thought he found that in the electrolysis of an aqueous, pure, chromic acid solution, metallic chromium separated at the cathode along with hydrogen, and that the amount of oxygen liberated at the anode was over one-third greater than one would expect from the amount of current used. This discovery Buff could not substantiate. The development of oxygen corresponded always to the Faraday law, and in the electrolysis of a 10 per cent. solution, the amount of liberated hydrogen did also."

As is evident in the words quoted, there is a criticism of Geuther's experiment only in so far as I indicated by the method of expression, that I considered a repetition of the experiment as desirable, which wish, after the discovery of Buff, was easily understood. In fact, on repeating the experiment, Messrs. Carveth and Curry also found that no excess of oxygen occurs

[1] Journal Physical Chemistry, 9, 231 and 353 (1905).

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at the anode, and it is entirely beyond explanation how, despite this fact, they come to the conclusion that "the criticism of Le Blanc on the work of Geuther needs radical change." I have certainly not taken the position that *all* that Guether observed was incorrect.

In what respect I have exercised an unjustifiable criticism of the work of Street, I have indeed been unable to find any explanation of in the article, and, in addition, in speaking of my patent, I have only given expression to a different view in one unessential point, which I now, as before, consider to be correct.

We come now to the most important case which concerns the patents of Placet and Bonnet. In these patents there is given a number of more or less definite formulas for the manufacture of metallic chromium. Certain experiments which I had carried out in my laboratory by Mr. Schick, following in the closest detail the statements of the patent, gave, at most, only traces of chromium precipitate. Other investigators had previously come to similar results, and they stand in complete contradiction to the statements of Placet and the French Academy of Sciences, according to which, in the electrolysis of an aqueous solution of chrome alum with the addition of alkali sulphate and some sulphuric acid, plating with chromium of any desired thickness, recalling in appearance oxidized silver, can be carried out. In the session referred to, Placet produced, in addition to chromium alloys, etc., a piece of metallic chromium of more than one kilogram weight. I came to the conclusion that the kilogram of chromium presented to the French Academy by Placet, had not been obtained in the way stated, or at least that the essential conditions for the production of a good chromium deposit had not been stated. Against the correctness of this conclusion, the gentlemen mentioned above took their position.[2]

I, therefore, should have expected to find the proof in the article referred to, that according to the directions of Placet, metallic chromium should actually be capable of being obtained in any desired thickness by the electrolysis of the aqueous solutions of chrome alum; this expectation, however, was not fulfilled, but it appeared, on closer examination, that (1) Messrs. Carveth, Mott, and Curry had not operated at all according to

[2] L. c., page 235.

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the directions of Placet and Bonnet, in so far as this had reference to the case before us; and that (2) the electrolyses had been carried through in so short a period of time that only a few mg., in specially favorable cases a few cg., of metal had been thrown down.

I must, therefore, assert in reply that the criticisms of my expressions were unjustified, and I must say that the expressions are as appropriate now as they were before. The possibility of obtaining good chromium deposits of any desired thickness under definite conditions I have never doubted, and the work of Neumann-Glaser has given us important suggestions therefor, which, indeed, the three gentlemen also made use of. The problem, however, is to-day still unsolved; at least we know of no researches which give directions for the production of chromium deposits of any desired thickness, which are so precise that one can make use of them. From the separation of a few mg. to its manufacture on an industrial scale, is still a long distance off and many notable difficulties have still to be overcome.

In order to satisfy myself as to what thickness of chromium deposits could be obtained by the discoveries which are before us, I have instructed Mr. A. Ruppert to supplement the work of Messrs. Carveth and Mott by undertaking several experiments in this direction, after a repetition of the different experiments of Carveth and Mott had given us a confirmation of quite a satisfactory degree. I add hereto the report of Mr. Ruppert, and would only remark that the experiments which follow have very little to do with the patents of Placet and Bonnet, inasmuch as they were carried out with solutions of different composition than those there given, solutions which we have found in recent years to be specially adapted *only* for the electrolytic separation of chromium.

According to the information obtained from the tables of Carveth and Mott, as well as from my own comparative experiments, I set before myself the problem to see if it were not possible to *separate out larger yields* of metallic chromium, because, in the experiments of the above-mentioned authors, only very small amounts, a few mg. of chromium, had been obtained. Therefore, continuous currents were sent through the electrolytes, whereby care was taken as far as possible to separate from each

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other those phases in which the current yield was best, that is, the intermediate ones. In these experiments, the condenser was removed, inasmuch as the temperature favorable for good yields became automatically established. From now on, moreover, for the first time, the chromium obtained was weighed, a thing which Carveth and Mott had not done in any of their experiments. I submit the results. Each series of experiments were carried out without change of electrolyte.

TABLE I.

Electrolyte consists of $Cr_2(SO_4)_3$; solution of sp. gr. 1.25, corresponding to a strength of 89 g. of chromium per liter.

(A). Cathode, brass rod of 12 sq. cm. surface, fixed; amount of cathode solution, 100 ccm.; diaphragm; anode solution, SO_4H_2, of sp. gr. 1.12.

Number of experiment	Current density in amperes per sq. cm.	Temperature. Centigrade.	Amt. of chromium obtained in grams.	Current yield in percentage.	Separated voltameter. copper in gm.	Duration in hours.	Remarks with reference to the metallic chromium.
1	0.5	35°	——	——	——	1	Crystalline, crumbling.
2	0.3	30-35°	0.374	21.1	3.200	1	Deposit of crystals, weighable.
3	0.2	30-35°	——	——	——	1	Adhering badly

(B). Same electrolyte and same electrode.

1	0.2	26-38°	0.408	7.1	10.354	4	As the deposit crumbled off, the current yield is much too small.

As in both experiments, the character of the precipitate is very poor and always crumbling, so that experiment "B," in fact, could not be carried to an end, I tested carbon cathodes in the form of arc lamp rods, which, for the sake of the better contact,

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I caused to rotate, whereby the passage of the current, as in the case of the collector of an electromotor, was effected by a sliding contact which proved itself to be satisfactory for the time. As the chromium sulphate which was formed in this case, could come in contact with the oxygen of the air, throughout its entire mass, because of the rapid stirring, I worked in a closed cell through which hydrogen gas was led.

TABLE II.

(A). The same electrolyte as before; rotating pencil of carbon = 20 sq. cm. surface; entire period of experiment, five and one-half hours.

Number of experiment	Current density in amperes per sq. cm.	Temperature. Centigrade.	Amt. of chromium obtained in grams.	Current yield in percentage.	Separated voltameter copper in gm.	Duration in hours.	Remarks with reference to the metallic chromium.
1	0.1-0.2	20-35°	——	——	——	½	Trifling precipitate.
2	0.1	36-38°	0.412	14.3	5.199	2	Crumbling; leafy.
3	0.1	35-38°	0.589	27.5	3.866	1½	Deposit of crystals.
4	0.1	36-38°	0.448	23.8	3.395	1½	Deposit of crystals.

(B). At higher temperature; entire period, five and one-half hours.

1	0.1	25-35°	0.1	3.8	4.744	2	Good; somewhat blackish.
2	0.1	35-52°	1.032	46.4	4.021	2	Good; somewhat blackish.
3	0.2	47-52°	0.089	4.9	3.287	½	Somewhat crumbling.

With the carbon electrodes, the adherence of the precipitate was in part better. Nevertheless, here also there were cases of crumbling off, as is seen above. I now endeavored to find the reason why, toward the end, in all the previous experiments

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both with the chloride and the sulphate solutions, the current efficiency always diminished.

Carveth and Mott thought that this could come only from an increased acidity in the cathode compartment, brought about by the diffusion of the sulphuric acid from the anode compartment, because with the small amount of metal which is taken away from the electrolyte, this concentration can only experience a very slight change.

Therefore, at that point in the electrolysis, when the current efficiency diminished, I put an excess of chromium hydroxide into the cathode compartment, with the supposition that as much might dissolve as corresponded to the amount of excess of acid present, while the chromium hydroxide remaining undissolved, would settle on the bottom. As the following experiments show, the desired end was achieved in this case.

TABLE III.

Same electrolyte as before. No passing in of hydrogen. In the case of No. 3, an addition of $Cr(OH)_3$; entire period, six and one-half hours.

Number of experiment	Current density in amperes per sq. cm.	Temperature. Centigrade.	Amt. of chromium obtained in grams.	Current yield in percentage.	Separated voltameter copper in gm.	Duration in hours.	Remarks with reference to the metallic chromium.
1	0.1-0.2	25-45°	0.713	18.2	7.099	2	Good; white.
2	0.2	40-57°	2.28	35.4	11.625	2½	Good; crystalline; somewhat crumbling.
3	0.2	45-62°	2.24	43.4	9.325	2	Leafy.

In the last experiment, I made the remarkable observation that when the chromium deposit was washed and at once dried with alcohol and gently heated, it gave off a very strong odor of ammonia. I had already noticed the development of this odor previously to this experiment, but at that time, I thought it was due to the carbon electrode. Now, however, when I tested

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the original sulphate for ammonia, I found that it was strongly ammoniacal, although the $Cr_2(SO_4)_3$ obtained from Merck should have been chemically pure. There remains, therefore, no doubt that electrolytic metallic chromium possesses a strong power of absorption for gases, which Carveth and Curry also found in their researches, "Electrolytic Chromium, II," namely, that it was capable of taking up about 250 times its volume of hydrogen. One can, perhaps, in certain cases, make use of electrolytic chromium as a catalyzer, to which I here call attention. It is indeed quite possible that the absorption of hydrogen (inasmuch as this is always set free in large amounts along with the metal), as well as the ammonia, is the cause of the brittleness and the scaling-off of the precipitate, although it is remarkable that thus far, and indeed in many cases later, under the same working conditions, I had obtained faultlessly smooth precipitates at least in very thin layers, where I otherwise obtained crumbling layers which adhered very badly.

The absorption of hydrogen and ammonia recognized above has no influence on the quantitative separation, but very probably upon the quality of the precipitate. In order to settle this, there was nothing left for me to do but prepare myself a chromium sulphate free from ammonia. I did this in the following way:

I dissolved pure metallic chromium with the aid of heat in dilute sulphuric acid, and neutralized the still-existing excess of sulphuric acid at the anode by means of $Cr(OH)_3$, free from ammonia. It was then evaporated to the desired degree of concentration, or, as the case might be, again diluted with water. Before I describe my experiments, carried out with these ammonia-free solutions, I will describe still another observation which Carveth and Mott made on solutions of $Cr_2(SO_4)_3$ electrolyzed and left in stoppered flasks quietly for a day, in which, naturally, there was very much $CrSO_4$. They say that these solutions after one day's standing gave off hydrogen. I was not able myself at first, after this short period of time, to notice any recognizable amount of hydrogen; but after keeping for eight days the solution which had been used, I could, on opening the glass stopper, ignite the hydrogen directly at the neck of the flask, in which case there was, moreover, a tolerably strong gas pressure. Both sulphate and chloride solutions show this phe-

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nomenon. The reaction takes place apparently according to the equation of ions

$$\overset{\cdot\cdot}{Cr} + \dot{H} = \overset{\cdot\cdot\cdot}{Cr} + H \text{ (given off)}.$$

Very probably it is possible under definite circumstances, as with the chloride, so with the sulphate, that the reverse change takes place, so that we have to do with reversible change,

$$\overset{\cdot\cdot}{Cr} + \dot{H} \rightleftharpoons \overset{\cdot\cdot\cdot}{Cr} + H.$$

From this consideration, it is also seen here that the yield diminishes with increased acidity. The chromous sulphate formed in the presence of acid is changed more quickly into chromic sulphate; the change takes place at higher temperatures more rapidly with chloride solutions, as was before shown, than with sulphate solutions, as is confirmed by experiment.

Now I turn again to my experiments with the ammonia-free $Cr_2(SO_4)_3$ solution, in which I found, to my surprise and astonishment, that even with this, a scaling-off cannot be avoided. Therefore, the previously-expressed view that the brittleness of the precipitates was to be ascribed to an absorption of ammonia, was not confirmed. It is true the absorption of the electrolytic hydrogen by the metallic chromium in active condition still came in question, yet we could not settle these matters by the present experiments. We must also, for the time being, therefore, conclude that the peeling off of the metal in thin scales is a specific property of the otherwise very hard and brittle electrolytic chromium, a property which was completely confirmed by previous workers.

The only promise of a way of improving the character of the precipitates was to try if small additions of organic and other substances would exercise a favorable influence. In this connection, I will cite here a passage from Foerster.[3] He writes there with regard to the form of electrolytic metallic precipitates as follows: "Very remarkable is the influence, often considerable, of many organic substances which exist in colloidal state in solution, of which frequently only traces suffice to change essentially the form of the metal separating at the cathode."

[3] "Electrochemistry of Aqueous Solutions," p. 202.

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And further, "the organic substances pass in traces into the electrolytic metal."

The following table gives the information with regard to the experiments which I made upon chromium sulphate solution.

TABLE IV.

The same electrolyte as before; the additions were made to every 100 c. c. of solution.

Duration of experiment in hours.	Material added, in grams	Current density in amperes per sq. cm.	Temperature. Centigrade.	Electrode	Character of chromium precipitate obtained.
1) 4	Sugar, 1	0.1–0.2	20-50°	20 sq. cm. surface fixed carbon.	Black; adherent.
1) ⅔	Oxalic acid, .5	0.4	20-55°	20 sq. cm. surface fixed carbon.	White; dull; adhering well.
2) 1	" " .5	0.1–0.2	40-47°	20 sq. cm. surface fixed carbon.	Good; white; smooth.
3) 2½	" " .5	0.2	45-55°	Brass, 12 sq. cm.	Good; white; crystalline.
1) 1¼	Benzoic acid, .5	0.1–0.4	20-70°	Fixed carbon, 20 sq. cm.	Black, crystalline deposit.
2) 1½	" " .5	0.1–0.2	25-40°	Fixed carbon, 20 sq. cm.	Black; poor.
3) 1	" "	0.2	40-50°	Rotating carbon 20 sq. cm.	Black; powdery.
1) 1	Salicylic, .5	0.4	25-70°	Fixed carbon, 20 sq. cm.	Black; crystalline.
2) ¾	" .5	0.1–0.2	34 52°	Fixed carbon, 20 sq. cm.	Black; crystalline; poor.
3) 1	" .5	0.1	25-30°	Rotating carbon 20 sq. cm.	Black; crystalline; poor.

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The only substances added where an improvement of the chromium precipitate was recognizable, was oxalic acid in an amount of .5 grams to the 100 c. c. of $Cr_2(SO_4)_3$ solution. On the other hand, with sugar, as well as with benzoic and salicylic acids in general, black, poor precipitates were obtained. These statements with regard to additions can also be found in the patents of Placet and Bonnet, with the statement that by means of them, most excellent results were obtained. Besides this, they made additions of boric acid in amounts from 5 to 10 grams per 1,000 c. c. of solution. In order to test the action of this, I made experiments in this line.

TABLE V.

Addition of boric acid to the electrolytes, 100 c. c.

Duration of experiment in hours.	Material added, in grams.	Current density in amperes per sq. cm.	Temperature. Centigrade.	Electrode.	Character of chromium precipitate obtained.
1	H_3BO_3; .1	0.3–0.5	25–62°	Fixed carbon.	Good, crystalline deposit.
2	" .1	0.2	30–48°	Rotating carbon	Good; white; somewhat dark
1	H_3BO_3; .5	0.3–0.4	36–62°	Fixed carbon.	Good; white; adherent.
1	" .5	0.2	45–55°	Fixed carbon.	Good; white; adherent.
1	" .5	0.2	40–52°	Rotating carbon	Good; white; adherent.

Here, therefore, by the addition of 0.5 g. of H_3BO_3 to the 100 c. c. of solution, a beautiful, smooth, white metal coating was obtained. For the experiments which were now to be carried on on a larger scale, therefore, a solution of this composition was used.

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Experiments on Larger Scale for Testing if It Is Possible to Obtain Thick Coatings of Chromium.

For this purpose I took a roomy electrolyzing vessel, in which, just as previously, a lead cylinder was used as anode in dilute sulphuric acid. The clay cell which was within this cylinder contained 400 c. c. of chromium sulphate solution in which two grams of H_3BO_3 were dissolved. As cathode, a copper rod of 40 sq. cm. surface was used. In this experiment, as also in some of the previous ones, I did not allow the cathode to rotate, because, on the one hand, the yield in the case of the stirring of the chromium sulphate solutions, particularly in the beginning, was injured rather than improved, and, on the other hand, the character of the precipitate was also smoother and more regular with the fixed electrode. Particularly the initial decreasing of the yield in the case of rotating electrodes in comparison with fixed, is *a priori* remarkable, because in other cases, stirring is generally favorable for the result of the electrolysis. The explanation of this is, however, very simple. It is that the initially-formed small amount of chromous sulphate, which forms the fundamental condition for the precipitation of the metal, by strong rotation of the electrode, is thrown off, so that it requires a long time until so much $CrSO_4$ is distributed through the whole solution, in order to obtain a good yield of metal. For this reason, I gave up the rotating cathode, and took the stationary one. Carveth and Mott also state this incidentally.

The quantitative determinations, both of the copper which was obtained in the voltameter, as well as the chromium precipitate, were made on the centigram balance, as we are now considering larger amounts.

I must further premise that the copper electrode, before the electrolysis, was acted upon for a short time by nitric acid, washed and cleansed of grease with potassium hydroxid, and finally repeatedly rinsed with distilled water, in order to obtain it absolutely pure and free from grease.

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TABLE VI.

Electrolyte 400 c. c. $Cr_2(SO_4)_3$ of the known concentration, with the addition of 2 grams of H_3BO_3. Copper cathode = 40 sq. cm. surface.

Number of experiment	Current density in amperes per sq. cm.	Temperature. Centigrade.	Amt. of chromium obtained in grams.	Separated voltameter copper in gm.	Current yield in percentage.	Duration in hours.	Remarks with reference to the metallic chromium.
1	0.1–0.2	30–48°	3.4	52.9	11.6	7	Only extremely thin deposit, smooth, later developing cracks.
2	0.2	25–45°	3.4	36.2	26.8	4	
3	0.15–0.2	38–50°	3.5	16.8	37.7	2	
4	0.15–0.2	42–50°	3.0	16.1	29.5	2	
5	0.15–0.2	25–48°	2.0	17.2	21.0	2	

The result showed that the chromium in thin layers, as had been obtained in the previous experiments, with the addition of H_3BO_3, was very beautiful and smooth, in fact could be polished, but so soon as a thickening took place, cracks formed in several places, which extended in different directions and finally led to a partial splitting off of the layer. Further experiments gave the same results.

In these experiments, it was also found that with large amounts of liquid, the gradual sinking of the current yield did not develop so greatly as before. Also, after at least twelve hours passage of the current, by testing the solution for acidity, a loss of this could be observed, rather than the increase noticed by Carveth and Curry, as well as by myself previously. The sinking of the current yield in Table V is probably attributable to a diminution in the concentration, because the solution, which at first contained about 36 grams of metallic chromium to the 400 c. c., had, for example in No. 3, sunk to a yield of 26 grams. Again, the adding of $Cr(OH)_3$ for neutralization of some free acidity present in a special group of experiments, did not result in a raising of the current yield after ten hours of continued electrolysis, a sign that the free acid was not present in any notable amount. The chromium hydroxid which was added, therefore, remained almost undissolved.

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From my own experiments, I can state that thin layers of chromium can be obtained perfectly smooth, and even capable of being polished and adhering most excellently to brass, carbon, and copper. The maximum thickness of this layer obtained by me can be calculated from Table VI, experiment No. 3, wherein 40 sq. cm. of separated chromium amounted to 3½ grams, the thickness therefore being 0.13 mm.

The formation of thicker layers and the production of large coherent masses of electrolytic chromium (I recall the kilogram of chromium of Placet), *are, however, so far prevented by the brittleness of the metal, and its tendency, when in thick layers, to develop fissures and cracks.*

Institute for Physical Chemistry
and Electrochemistry of the
Polytechnic School at Carlsruhe.

DISCUSSION.

PRESIDENT BANCROFT: I call attention again to the samples of chromium which were shown at Boston last year, and must express a certain regret that Le Blanc should not have put more time on the question of depositing chromium from chromic acid. The work with chromium sulphate and chromium chloride showed that only under great precautions could one get a satisfactory deposit of chromium. The real solution from which to deposit chromium is not chrome alum nor chromium sulphate, it is chromic acid. When you were inspecting the laboratory the other day we made some chromium before your eyes. I cannot believe that it is impossible to plate that chromium to any desired thickness. If the solutions remain unchanged and the conditions remain unchanged you are bound to get the deposit to any thickness you please. That has been shown perfectly satisfactorily in regard to nickel. People make statements that you cannot precipitate nickel to more than infinitesimal thickness. You cannot if you do not keep the conditions constant. You can deposit to any thickness you please, and a chromic acid solution is an ideal one in which to keep the bath perfectly constant. So far as I

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know, no one here has ever plated chromium to the thickness of one inch, but I feel certain that it is merely a question of power to do it. If there is any real inducement to plate chromium an inch thick, we will do it.

MR. H. E. PATTEN: About 1902, working in Prof. Burgess' laboratory, Mr. A. B. Marvin and I tried to reproduce the conditions for depositing chromium given at that time. We failed utterly. We could not get anything to equal them at all.

PRESIDENT BANCROFT: You are not the only person who has had similar difficulty trying to reproduce the results in Neumann's paper.

MR. CURRY: We ran some few plates and made long runs, and we had chromium deposits that were very good. They were more than a millimeter in thickness, which is more than six times as thick as Prof. Le Blanc says that he could plate. We did not make but two or three of those deposits; but so far as we tried it we were very successful.

MR. CARVETH: In all the experiments which Mr. Curry and myself have made with chromic acid, to get good platings, we used a single compartment cell. The electrolyte was delivered at the cathode, went over the cathode around over the anode, and made a continuous circulation. You might then have a far better chance of obtaining thicker deposits.

MR. CARRIER: I would like to emphasize the whole tone of the paper. I think it was Prof. Le Blanc's idea to develop a commercial process for the manufacture of electrolytic chromium; while I think the other experiments have been more concerned in obtaining good chromium coatings. What he desires to do is to produce metallic chromium in the same way that Prof. Burgess has produced electrolytic iron.

(Communicated after Adjournment.)

DR. H. R. CARVETH: To the conclusions drawn by Carveth and Curry from their study of chromic acid solutions, LeBlanc replies by a criticism of experiments made by Carveth and Mott with chromic sulphate and chloride.

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Our original plan of work covered three subjects, of which the first two only were completed; this was because two of the authors entered technical work. The third paper in which it had been the intention to check more carefully the experiments of Schick in so far as he aimed to duplicate the work of Placet and Bonnet, was but started. A few runs showed that with other conditions the same as used by Schick, but with higher current density, the metal could be deposited, and that the statements of Placet and Bonnet were probably correct. These unpublished results influenced us, but were not responsible for our criticism.

The latter deals rather with LeBlanc's comments on chromic acid electrolysis; we do not take our position merely on the ground stated in the paper under discussion.

In passing, we shall merely repeat that Carveth and Mott did weigh their chromium—see their article on page 239.

There is no doubt that Guether was the first to discover that chromium could be deposited by electrolysis of solutions of chromic acid. Would LeBlanc give Guether credit for this?

The general attitude of LeBlanc toward Placet and Bonnet is shown on page 9 of the Monograph, where he states that their patent claims in the majority of cases deal with fantasies and not with experimental work done. We have stated in regard to the Placet-Bonnet American patent of 1894 that "the specifications are in all probability more complete than those of the earlier European patents." Of the electrolytes used by them, they state that "the most important of these compounds is chromic acid." As to yields—"metallic chromium is produced in sufficient quantity and with sufficient economy to constitute an industrial process." The work done by Carveth and Curry showed that these claims were not fantasies, and indicated that other workers had failed to obtain results because they used too low current densities. These inventors continually insisted, as we have pointed out, upon the use of high current densities. Does LeBlanc consider these claims phantasies?

LeBlanc tried to reproduce conditions given in the paper read before the French Academy by Placet. In this paper, concentration, temperature, and current density were not indicated. Practically no chromium deposit was obtained by LeBlanc. His

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criticism was: "There can therefore be no doubt that the kilogram of chromium presented to the French Academy by Placet was not obtained in the way stated, or that at least the conditions necessary to obtain good precipitate of chromium are not given there." The second conclusion is certainly obvious, when it is remembered that details as to nature of one electrolyte, the concentration, temperature, and current density, are not given at all. Fairness would demand that the first criticism be omitted until some of these variables had been examined. The first one suggested would be high current density. A bath made by dissolving 15 grams of chrome alum and 15 grams potassium bichromate in 100 grams of water, gave Schick only traces of metal at a current density of 20 to 30 amperes per square decimeter. M. F. Gallup, with the same electrolyte but with a density of 40 to 60 amperes and temperature of 40° to 60°, obtained good deposits.

The author concludes that the peeling of the metal is a specific property of the otherwise very hard and brittle chromium. The evidence from which the conclusion is drawn is very weak. We have made deposits very much thicker and of greater weight than any shown by LeBlanc, and these were exhibited at the Ithaca and Boston meetings.

That it is a long distance from the separation of a few milligrams, to the preparation of an industrial scale, no one doubts; but in this case, difficulties come, not so much from the method as from the economical side.

(Communicated after Adjournment.)

DR. M. LEBLANC: With reference to the foregoing discussion, I have to remark the following, passing by everything of secondary importance.

1. With reference to the case of Geuther, I beg to refer to that already said by me, and have nothing more to add to it.

2. Messrs. Carveth, Mott, and Curry, in their two articles, specially antagonized my judgment on the report of Placet made to the French Academy. It was distinctly emphasized in this

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report, that a chrome alum solution was used for electrolysis. I have established that the two articles referred to furnish no points from which we can find that metallic chromium can be obtained in any desired thickness from such solutions. Therefore, they furnish no contribution to the passing of a judgment upon the above-mentioned report. This matter established by me has not been contradicted in the discussion.

3. The task of Mr. Ruppert was not, as it appears to have been thought, to find a process for the preparation of chromium deposit of any desired thickness, but to test if from chromic salt solutions, taking Placet's report as a basis, with the aid of what advances have become known in the meantime, chromium deposits of any desired thickness could be obtained. I desire to emphasize this specially, because in my report it was not sufficiently clearly expressed. With this, all reference to chromic acid solutions are settled.

4. I have stated that I do not doubt that some day it will be possible to obtain chromium in any desired thickness, but that at the present time, there is no method given for this, and the discussion has confirmed this. At the same time, the opinion seems to prevail that the preparation of homogeneous deposits of any desired thickness would follow naturally when one first got to the point of obtaining thin homogeneous deposits. On the basis of my experiences, not only with chromium, but also with other metals, I do not coincide with this view; the preparation of a homogeneous deposit of any desired thickness, with execrescences, holes, etc., is, for the most part, notably more difficult.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

LECTURE-ROOM SWITCHBOARD.

By WILDER D. BANCROFT.

We have recently installed a switchboard for lecture purposes which enables us to show a great number of experiments involving currents up to twenty amperes and voltages up to thirty volts. The switchboard has proved so serviceable for lectures on applied electrochemistry that I venture to describe it. The instruments are a Weston Type L Ammeter with a double scale reading to twenty amperes and to two amperes, and a Weston Type L Voltmeter with a double scale reading to thirty volts and to three volts. The dials can be illuminated from the back, though we rarely find it necessary to do this. Since the scales are twenty-eight inches in length, 0.1 ampere is 1.4 inches on the lower scale and 0.1 volt is nearly one inch. Even smaller changes of current or voltage can therefore be seen from all parts of the room, which is a small one seating about fifty-five students. For a lecture-room seating two hundred students I should be tempted to put in Type M instruments which have a thirty-six inch scale.

Our storage battery system consists of five groups of cells giving 8, 4, 8, 2 and 6 volts respectively. Six wires run from these five group of cells, making it possible to throw all five groups or any combination of adjacent groups in series. We can thus get voltages of 2, 4, 6, 8, 10, 12, 14, 16, 20, 22 and 28 volts at the switchboard, assuming two volts to each cell. On the lecture table are two sets of seven binding-posts, each set corresponding to the six battery leads and to the ammeter lead, to which reference will be made. By having two sets of binding-posts crosswise to the table the lecture assistant can set up experiments to the right and left of each set of binding-posts, thus utilizing the whole surface of the table with a minimum of temporary wiring. The same effect could have been obtained by running seven bare wires lengthwise of the table; but this would have taken up more space

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when experiments were not being shown. Personally, I doubt whether such an arrangement would be satisfactory in any case.

Five of the battery leads pass to the pivots of the double-throw switches, 1, 2, 3, 4 and 5 respectively in Fig. 1. The five outer ends of these switches are connected through the resistances R1, R2, R3, R4 and R5 respectively to the voltmeter plugs, 1, 2, 3, 4 and 5, thence to binding-posts, 1, 2, 3, 4 and 5 on the lecture table. The sixth battery lead, which is the cathode wire for the last group of cells, passes through the resistance R6 to voltmeter plug 6 and thence to binding-post 6 on the lecture table.

The inner ends of the double-throw switches 1-5 are all con-

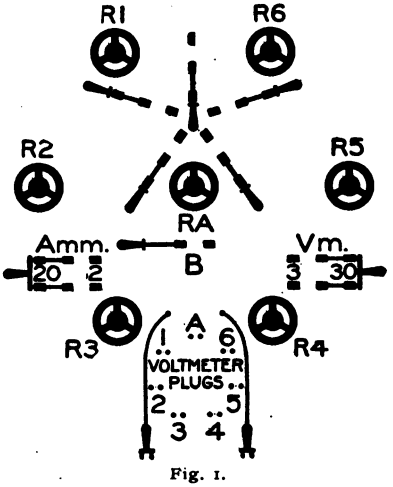

Fig. 1.

nected together and a lead passes from them through the ammeter resistance RA to the pivots of the double-throw ammeter switch, thence to the voltmeter plug A and from there to a binding-post A on the lecture table. The five double-throw switches are made interlocking so that only one can be thrown to the center at a time, thus preventing all possibility of short-circuiting the batteries. In the switchboard as built these are single-pole switches; but they would have been more durable if they had been double-pole switches.

The double-throw switches on the left, marked "20 Amm 2," throw in the 20 ampere or the 2 ampere scale. The corres-

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ponding switch on the right, marked "3 Vm 30," throws in the 3 volt or the 30 volt scale while the switch B in the middle short-circuits the ammeter. From the pivots of the double-throw voltmeter switch flexible cords pass through the switchboard and connections are made by inserting the terminals in the voltmeter plugs A-1-6. Of course the voltage shown on the voltmeter is the difference of potential at the pivots of the voltmeter switch and not at the terminals of the electrolytic cell. Since No. 8 wires run from the switchboard to the lecture table, this error is small in most cases and the general compactness of the arrangement is more important than the highest degree of accuracy.

The resistances are Ward-Leonard Field Rheostats mounted on the back of the board. The resistances R1-R6 are each 15 ohms and have sixty steps. The resistance RA has 7.5 ohms and sixty steps. The switchboard itself is four feet four inches wide by three feet ten inches high. It is mounted on iron pipes away from the wall so that it is possible to get behind it to remedy defects in the wiring, etc. The voltmeter and ammeter are not mounted on the switchboard but are placed in the center of the rear wall of the lecture room above the black-boards.

When the double-throw switches 1-6 are thrown with the handles pointing away from the center, binding-posts 1-6 can be used without any current flowing through the ammeter. By throwing the handle of any switch, 1 for instance, to the center, the ammeter is thrown in circuit. By making the connections on the desk at A and 2, 3, 4, 5 or 6, we get the first, the first two, the first three, the first four, or the whole five groups of cells in series with the ammeter. The amount of current flowing through the electrolytic cell can be regulated by means of the resistances. If we leave the voltmeter circuit closed and break the ammeter circuit, we get the counter-electromotive force of the polarization cell, subject, of course, to correction for the relative internal and external resistance. If a primary cell be substituted, its voltage can be shown. On connecting any of the inner ends of the double-throw switches 1-5 by means of a wire to the proper end of the voltmeter switch, both the current and voltage of a primary cell can be shown.

With a double-pole, double-throw switch on the desk, it is possible to throw the polarizing current first one way and then the

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other through an aluminum rectifier, showing a high voltage with very little current in one case, and a low voltage with a high current in the other. With two copper electrodes in an acidified copper sulphate solution, heating the solution will easily make a difference of several tenths of a volt in the voltage necessary to cause a given current to pass, and one-tenth of a volt is nearly an inch on the voltmeter scale.

One very instructive experiment is to have two copper electrodes in a long tank of acidified copper sulphate solution. When the electrodes are moved closer together, the current increases even though the voltage falls. To make this succeed, the resistance in the switchboard circuit must not be too small in comparison with the maximum resistance of the tank. Otherwise, we shall get the other, equally instructive but not so unexpected, experiment of the voltage remaining nearly constant while the current increases. If a variable metallic resistance be substituted for the copper sulphate solution, this experiment can be used to show the distinction between electromotive force and potential differences for cells with and without high internal resistance, by considering the resistance in the switchboard as part of the internal resistance of the battery.

If the handle of switch 1 be thrown to the center and a wire be connected from the pivot to the outside connection, the binding-posts A and 1 on the desk will both be "live." On placing an electrolytic cell across A and 1, and connecting 1 with any other binding-post, we shall have the ammeter and the electrolytic cell in a shunt circuit and we can show decomposition voltages to a class provided we make the electrodes so large that the residual current is nearly 0.01 ampere.

Many other experiments could be cited but these are enough to show the flexibility of the apparatus.

I am indebted to Mr. G. B. Upton for getting the switchboard into so compact a form and for the working drawings.

Cornell University.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

THE FREE ENERGY OF SOME HALOGEN AND OXYGEN COMPOUNDS, COMPUTED FROM THE RESULTS OF POTENTIAL MEASUREMENTS.

By M. DeK. Thompson.

INTRODUCTION.

One of the most important chemical problems of the present time is the determination of the free energy of formation of compounds from their constituents, for it is this quantity and not the heat evolved that is the true measure of chemical affinity. No reaction can take place of itself that is not capable of doing external work, and the maximum amount of such work which a reaction can produce at any constant temperature is called the free-energy-decrease of the reacting system. Although this is a vastly more important quantity than the heat evolved by the reaction, it is one which is known in few cases, compared with those for which the heat-effect has been measured. This is partly due to the greater difficulty of determining the value of the free-energy change, and partly to the fact that its importance has not until recently been generally appreciated. Just as in thermochemical investigations, so here the most fundamental data are the free energy changes attending the formation of various chemical compounds out of their elements, for from these data the free-energy change attending any reaction can be calculated by direct summation.

One method of measuring the free-energy change of a reaction is to determine the conditions of chemical equilibrium. For a reaction of the general type, $aA + bB.... = eE + fF.....$ the work W producible by the conversion of a mols of A and b mols of B at concentrations C_A', C_B' respectively into e mols of E and f mols of F at concentration C_E', C_F' respectively, or the free-energy decrease $-\triangle F$ attending it, is given by the equation

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$$W = -\triangle F = RT\left[\log_e K - \log_e \frac{C'^{e}_{E}\, C'^{f}_{F} \ldots}{C'^{a}_{A}\, C'^{b}_{B} \ldots} + (e+f\ldots - a - b\ldots)\right]$$

in which K is the equilibrium-constant defined by the equation

$$K = \frac{C^{e}_{E}\, C^{f}_{F} \ldots}{C^{a}_{A}\, C^{b}_{B} \ldots} \quad \text{where } C_A, C_B \ldots C_E, C_F \ldots$$

are any concentrations at which equilibrium prevails. In numerous cases, however, it is impossible to determine the equilibrium constant, and therefore it is fortunate that another method is applicable to many reactions—one based on electrical potential measurements.

If the saturated solution of a salt in contact with the salt in the solid phase be electrolyzed at constant temperature between electrodes consisting of the products of decomposition, and if the process be reversible, the work done is that necessary to decompose the solid salt[1]. Conversely, the energy obtainable from this combination when working reversibly as a voltaic cell, is the free energy of formation of the solid compound from its constituents. What the solvent is makes no difference in either case, provided it is not decomposed by the electrodes themselves. The solvent might be pure water, or a solution of some other salt in water, or any other liquid, so long as it is saturated with the salt in question. To take a concrete example, the free-energy change attending the formation of silver chloride could be determined either by measuring the decomposition point between platinum electrodes of a saturated solution of silver chloride in water, or by measuring the potential of the cell. Ag/Sat.sol. of AgCl/Cl_2. If the cell is reversible, the two results should be identical. The latter is much the more accurate of the two methods, on account of the arbitrariness that generally accompanies the determination of decomposition points.

The free-energy decrease in any such case attending the formation of one formula weight of the solid salt out of its

[1] Bodländer, Z. phys. Chem., *27*, 55 (1898).

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elements is simply the product νEF where ν is the number of equivalent weights in one formula weight; E is the electromotive force of the combination, and F the quantity of electricity whose passage, by Faraday's law, always attends a reaction involving one equivalent. If E is expressed in volts and F in coulombs (when it has the value 96,600) the free energy will, of course, be in joules. The negative value of this product may be called simply the free energy F of the salt, that of the elements being taken as zero; and we may write, therefore: $F = -\nu EF$. In case, however, one or more of the elementary substances or the resulting compound is gaseous, and $\triangle N$ mols of gas are produced in the formation of one formula weight of the substance, the free-energy equation becomes $F = -(\nu EF + \triangle NRT)$

The electromotive force of the above-mentioned type of cell is, however, made up of the electromotive forces at the two electrodes. Now, in many cases, these separate values involved have been measured against some standard electrode for one purpose or another, and are found scattered through the literature. It is the aim of this article to summarize these results, to unite them, making a suitable correction for the potential-difference of the liquid-liquid couple, so as to give the electromotive force of a cell composed of the elementary electrodes and a saturated solution of salt in question, and to calculate therefrom, as just described, the free energy of the salt itself. The available data relate mainly to difficultly soluble salts, for the potential difference of *saturated* solutions against electrodes have, as a rule, been measured only in the case of such salts. The necessary data also exist for a few gaseous or volatile hydrogen compounds (hydrochloric acid, water and ammonia), and computations have therefore also been made for these substances.

The details of these computations will appear in the *Journal of the American Chemical Society,* so that they may be omitted here. It may be interesting, however, to explain by means of an example how the data were worked up. Let us consider the computation of the free energy of silver chloride. A table was made of the values of all the couples of the type Ag/solid AgCl + solvent, that could be found. They were, of course, measured against some other couple whose value is known. Very often this other couple was the "normal electrode," but not always. Then the

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values of all the chlorine couples were tabulated. These were of the type Pt + Cl_2/Cl_2 + solvent, with the gaseous chlorine at atmospheric pressure. The couples which had the same solvent were then paired by taking the algebraic difference of their separate potentials, and the electromotive forces of the cells of the type: Ag/AgCl + solvent/solvent + $Cl_2|Pt + Cl_2$ obtained. In case the same couple had been measured by different observers, these values were first averaged before combining with the opposite couple.

The free energy of one mol consisting of N equivalents, of an n-ionic solid compound may also be calculated from the electrolytic potentials E_C and E_A of its elements (of which let N be gaseous), and from the solubility S of the compound (expressed in equivalents per liter and regarded as completely ionized) by the following formula, which in somewhat different form was first derived by Bodländer[2].

$$-F = (E_C - E_A)\, N\, F - nRT \log S - NRT$$

It is therefore of interest to compare the results obtained in this way with those computed above, directly from decomposition-potentials of the saturated solutions.

For this purpose, the electrolytic potentials for the metals are taken from Wilsmore's paper.[3] With respect to the non-metals

[2] l. c.—The above formula may also be deduced by the following reversible process, in which one mol of an n—ionic salt, consisting of N equivalents, is formed from its elements, of which N mols may be gaseous.. Make use of a cell consisting of the elementary substances as electrodes dipping into a normal solution of the corresponding ions. Let this cell act reversibly until N equivalents of the elementary substances have gone into solution as ions, at the same time adding to the solution reversibly the quantity of water necessary to keep the concentration constant. The work done by the cell in this process is:

$$(E_A - E_C)\, NF - NRT + nRT$$

Now allow the salt to change its concentration to that corresponding to its solubility S (by cutting off the quantity of solution which contains one mol and diluting it); assuming it is completely dissociated in both solutions, the work done by the system in this process is $nRT \log \frac{1}{S}$ Now force the salt out of solution by means of a semipermeable piston, in which the work done by the system is $-nRT$. The total work done by the system is therefore

$$(E_C - E_A)\, NF + nRT \log \frac{1}{S} - NRT$$

[3] Since Wilsmore uses the word "normal" in the sense of "molal," his values for all except univalent metals must be corrected. This has been overlooked by several authors who have copied his data.

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it is important to note that in the case of all elements whose concentrations in the electrode can be varied, such as the halogens and oxygen, there are two kinds of specific electrolytic potentials—one, where the solution is saturated with respect to the element in question; the other, where the solution is molal with respect to it, the solution being molal with respect to the ions of the element in both cases.[4] It is evident the former is the proper one to employ in these computations. For computing the electrolytic potential of chlorine, Sullivan's[5] value of the equilibrium ratio for the reaction, $Cl_2 = 2Cl^- + 2F^+$, has been adopted. The value of the solubility of chlorine in pure water is 0.089 mols per liter at 25°. It would, however, be less in a solution normal with respect to chloride ions. There is good reason for the assumption that in a normal potassium chloride solution, the solubility at 25° would be only 81 per cent. of the above amount,[6] and for a solution normal with respect to chloride ions, the reduction in solubility would probably not be much greater. Therefore, the solubility is taken as 0.072 mols per liter. The resulting value of the electrolytic potential differs by one millivolt from the value computed by Haber.[7]

In computing the electrolytic potential of bromine with respect to a solution saturated with bromine molecules, the solubility is taken the same as in pure water, 0.2125 mols per liter at 25°. By means of this datum, the electrolytic potential, with respect to a solution saturated with bromine molecules, is computed from the electrolytic potential used above, in respect to a solution molal with bromine molecules. The electrolytic potential of iodine is computed from Crotogino's measurements, which are also the basis of the values of the iodine couple used in the previous method.

The following table gives the results of this computation:

TABLE I.

The electrolytic potentials of the halogens in solutions saturated with respect to the halogen molecule. t. = 25°.

[4] See Haber, Z. Elektrochem., 7, 1047 (1901).

[5] Z. phys. Chem. 28, 523 (1899) $\log_{10} K = 56.756$.

[6] Jokowkin, Z. Phys. Chem. 29, 637 (1899)

[7] l. c.

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$$E_{Cl_2} \quad -1.643$$

$$E_{Br_2} \quad -1\ 358$$

$$E_{I_2} \quad -0.817$$

The values of the solubilities are taken from the third edition of Landolt-Börnstein-Meyerhoffer's Tables, and only those are used which are not based on measurements used above, so as to avoid working in a circle. The results are given in column 4 of table V.

THE FREE ENERGY OF MERCURIC CHLORIDE, BROMIDE AND IODIDE.

If the equilibrium between a metal and two of its halides in different states of oxidation is known, the free energy change attending the decomposition of the lower halide into the higher halide, and the metallic element may be computed, and this combined with the free energy of the lower halide gives that of the higher one. The necessary data exist in the case of the mercury halides, since the concentration of the mercuric halides (as such) in equilibrium with the solid mercurous halides and mercury has been indirectly determined by Sherril.[8] If that concentration be designated by C and the solubility of the mercuric halide (regarded as unionized and unassociated) by S, then the work producible by the reaction

$$Hg_2X_2(\text{solid}) = Hg + HgX_2(\text{solid})$$

may be readily shown[9] to be $RT \log \frac{C}{S}$. And evidently the algebraic sum of this quantity of work and of that attending the production of one formula weight of Hg_2X_2 out of its elements is the free energy decrease attending the formation of one formula weight of HgX_2 out of its elements.

[8] Z. phys. Chem. *47*, 103 (1904)

[9] In a reaction mixture consisting of mercury and solid mercurous halide in equilibrium with an aqueous solution of mercuric halide of concentration C let one formula weight of solid Hg_2X_2 decompose into mercury and (dissolved) HgX_2 the latter being simultaneously removed at the same concentration into pure water through a wall permeable for it alone. The work produced hereby is RT. Now concentrate the HgX_2 solution so obtained till its concentration becomes S, that of a saturated solution: the work produced is $RT \log \frac{C}{S}$ Finally force the salt out of the solution in the solid state; the work produced is $-RT$. The total work is therefore $RT \log \frac{C}{S}$

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The values of the quantities C and S given by Sherrill, of the calculated quantity of work $RT \log \frac{C}{S}$ and of the free energy in calories or mercuric chloride ($F\mathrm{HgX_2}$) are given in the following table:

TABLE II.

FREE ENERGIES OF MERCURIC CHLORIDE, BROMIDE AND IODIDE.

Substance.	$C \times 10^6$ in Mols per l.	$S \times 10^3$ in Mols per l.	$RT \log \frac{C}{S}$	$F(\mathrm{HgX_2}) \times (-1)$
$HgCl_2$	2.9	260.	—6750	42,600
$HgBr_2$	1.4	17.	—5250	37,300
HgI_2	4.0	0.13	—2060	24,100

HYDROGEN | LIQUID WATER | OXYGEN.

The best value for the electromotive force of this cell seems to be 1.22 volt at about 20°.[10] The corresponding value of the free energy of one molecule of water calculated by the equation

$$F = -\left(2EF - \tfrac{3}{2}RT\right) \text{ is } -55{,}500 \text{ calories.}$$

HYDROGEN | HYDROCHLORIC ACID | CHLORINE.

The formula that applies to a solid in contact with its saturated solution applies equally as well to a gas in equilibrium with its solution (it being understood that $\triangle N$ represents the increase in the number of mols of gas attending the reaction). Thus, if we have a hydrogen and a chlorine electrode in normal hydrochloric acid, the electromotive force of this cell would give the free energy of hydrochloric acid at a pressure equal to its partial pressure over its normal solution, referred to hydrogen and chlorine at atmospheric pressure. The term $\triangle N$ becomes zero, as there are as many mols of gas before as after the reaction has taken place. If, however, we wish to know the free energy of hydrochloric acid at atmospheric pressure, referred to hydrogen and chlorine at atmospheric pressure, then the free energy computed from the voltage must be diminished by $RT \frac{76°}{p}$,

[10] Lewis, J. Am. Chem. Soc. *28*, 158, (1906).

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where p is the partial pressure in millimeters of mercury of hydrochloric acid over the solution in question. The necessary measurements of vapor and electromotive force have been made for hydrochloric and hydrobromic acids but not for hydriodic acid. The free energy of hydriodic acid could be computed however, from the data on the dissociation at high temperatures. See Bodenstein, Z. phys. Chem. *29*, 295, (1899). Dolezalek[11] has measured the cell $H_2|HCl|Cl_2$ at 30° and at different concentrations. He has also measured the partial pressures of hydrochloric acid at the same temperature, for different concentrations. The following table contains the results, and in the last column the free energy computed from them:

TABLE III.

Normality of HCl Solution	Partial Pressure of HCl in m.m of Hg 30°	Volts	Free Energy ×(−1) of one mol HCl in Calories at 30°
4.98	0.24	1.190	22,800
6.43	0.69	1.147	22 400
11.20	134.	1.005	22,200
11.62	189.	0 999	22,300
12.14	313.	0.981	22,100
12.25	337.	0.974	22,000

The average value is 22,300 calories, 0.5 per cent., at 30°. The heat of the reaction at 18° is 22,000 calories,[12] which varies very slightly with the temperature. It would be practically the same at 30°. The temperature coefficient of the free energy at 30° is then $\frac{dF}{dt} = \frac{F-U}{T} = 1\ 07$ calories per degree. The free energy at 18° would then be only 1.8 calories less than at 30°. This correction is, therefore, negligible.

HYDROGEN | HYDROBROMIC ACID | BROMINE.

Measurements of the above cell have been made by Bodenstein and Geiger at 30°, (see Z. phys. Chem. *49*, 70, 1904), and the vapor pressures of the hydrobromic acid over the solutions as well as of the hydrogen and the bromine. The bromine couple was not saturated with bromine. The electromotive force of this cell gives the free energy of hydrobromic acid at the partial pressure

[11] Z. phys. Chem. *26*, 321 (1898).
[12] Ostwald, Lehrbuch d. allg. Ch., 2nd Aufl., Bd. II, 1. p. 103.

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measured, formed from gaseous bromine and hydrogen at the measured pressures.

If we start with gaseous bromine at atmospheric pressure (assuming this degree of supersaturation could be realized) this must be expanded to the pressure at which it exists in the cell. The work done by the system will be $\frac{1}{2} RT \log_e \frac{760}{p_{Br_2}}$ for one-half of a mol. Allowing the hydrogen to change from atmospheric pressure to that measured, the work done by the system will be $\frac{1}{2} RT \log_e \frac{760}{p_{H_2}}$. Now compressing the acid to atmospheric pressure, the work done by the system will be—$RT \log_e \frac{760}{p_{HBr}}$, and hence the free energy is given by the formula—$F = E \times 23090 + RT \log_e \frac{p_{HBr}}{(p_{Br_2})^{\frac{1}{2}}(p_{H_2})^{\frac{1}{2}}}$

The final column of the following table gives the results of this computation:

TABLE IV.

Partial pressure of H Br. in m. m. of mercury.	Partial Pressure of Br_2 in m. m. of mercury.	Partial Pressure of H_2 in m. m. of mercury.	Electro-motive force in volts	Free energy × (—1)
12.0	0.682	742.5	0.573	12850
2.25	1.509	753.6	0.625	12800
1.19	1.448	760.6	0.636	12680

The average value is 12,800 calories at 30°. The difference in the heat capacities at constant volume of one mol of hydrobromic acid and of its constituents is 1.06 calories (obtained from Landolt-Börnstein-Meyerhoffer's Tables). The heat of the reaction is, therefore, practically the same for 30°. In order to get the free energy at 18° we may substitute the known values in the integrated Second Law equation given below (see under Ammonia). This gives $F = -11950$ cal. at 18°.

HYDROGEN | AMMONIA | NITROGEN.

The cell Pt + H_2|solid NH_4NO_3 + solution of NH_4NO_3 in NH_3|Pt + N_2 has been found to be reversible and to have at —10° an electromotive force of 590 millivolts.[18] The partial

[18] Baur, Z. anorg. Chem., *29*, 305 (1902).

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pressure (p) of the ammonia over this mixture has been found to be 240 mm. at —10.5°.[14] Now the free energy (F) of one mol of gaseous ammonia at atmospheric pressure referred to its elements at atmospheric pressure (p_o) is given by the expression

$$-F = 3\,EF - RT + RT \log \frac{p}{p_o}$$

from which, by substituting the above values, one finds at — 10°, F = —39,700 calories.

In order to obtain from this free energy at 18°, we may employ the Second Law equation, $-\frac{dF}{dt} = \frac{U - F}{T}$ which, integrated under the assumption that the energy change (U) attending the reaction is constant, gives

$$\frac{F_2}{T_2} - \frac{F_1}{T_1} = -U\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

U, however, has the value 11,420 cal. at 18° and 11,280 cal. at— 10°, or an average value of 11,350 cal.[15] Putting F_1 = 39,700, T_1 = 263 and T_2 = 291, we find for F_2 (whose value is the free energy of one mol gaseous NH_3 at 18° and 1 atm. pressure) the value of 45,200 cal.

This result may be compared with that obtained by using the equilibrium constant of the reaction in question recently obtained for the temperature 1020° by Haber and Van Oordt, (Z. anorg. Chem. *44*, 341, 1905). At this temperature, this constant, which is defined by the equation

$$K = \frac{(p_{N_2})^{0.5}\,(p_{H_2})^{1.5}}{(p_{NH_3})}$$

has, when the pressure is expressed in atmospheres, the value 2706. From this value the work producible by the reaction

$$0.5\,N_2 + 1.5\,H_2 = NH_3$$

[14] Kuriloff, Z. phys. Chem., *25*, 108 (1898).
[15] Ostwald, l. c., p. 139.

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when it takes place from left to right and when each gas is at atmospheric pressure is calculated by the equation given in Section I of this article to be -23,000 cal. By means of the heat of reaction and heat capacity data cited by the authors and the integrated form of the Second Law equation given by them the work produced may be computed for any other temperature. For 18° it is found to be + 5100. Hence we have for the free energy of one mol of ammonia $F = -5100$ cal.

This result is evidently utterly inconsistent with the value deduced from potential measurements. The most probable explanation seems to be that there is an error in the interpretation of the potential values arising from the fact that the potential observed was not determined by the solution-tendency of nitrogen at all, but by some other reaction in the solution. Nitrogen is a very inert gas, especially at low temperatures; and therefore this seems a reasonable explanation. There does not seem to be any corresponding possibility of a large error in the computation involving the equilibrium constant, and it is probable that the value of the free energy deduced therefrom is at least an approximate one. Both are given in Table VI.

SUMMARY OF THE RESULTS.

The results of the above-described computations, as well as certain other related data, are presented in Table V. Column 2 contains the free energies of the chlorides referred to, gaseous chlorine at atmospheric pressure. These values are here collected from the various preceding tables. By adding $N\ R\ T$ to these, the values in column 3 for the chlorides are obtained, which show what their free energies would be if the chlorine were liquid or solid at the temperatures in question. The previously computed free energies of bromides and iodides are also given in this column. The free energies computed from solubilities are given in column 4. The values that deviate widely from those in column 3, which is the case with the most difficultly soluble compounds, where the error in determining the solubility is large, are placed in brackets. The next three columns contain the values of the total energies, all of which are taken from Landolt-Börnstein-Meyerhoffer's

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TABLE V.

THE FREE AND TOTAL ENERGIES OF THE SOLID HALIDES OF SILVER, MERCURY, COPPER, THALLIUM AND LEAD AT ABOUT 18°.

Compound	Free Energy×(−1).			Total Energy×(−1).			Ratio of Free to Total Energy.		Solubility in Equivalents per Liter at 20°.
	Halogen, Gaseous, at atmos. pres.	Halogen, Liquid or Solid	Halogen in Usual State, Computed from Solubilities.	Halogen, Gaseous.	Halogen, Liquid.	Halogen, Solid.	Elements Solid	Elements in Usual State.	
1	2	3	4	5	6	7	8	9	10
AgCl	25,600	25,900	26,800 [6]	28,900	26,700	(25,400)	1.02	0.89	1.06×10^{-5}
AgBr	. . . . .	23,000	23,900	. . .	23,400 [1]	(22,100)	1.04	0.98	5.1×10^{-7}
AgI	. . . . .	15,900	[26,300]	. . .	. . . . .	14,200 [1]	1.12	1.12	1.5×10^{-8}
CuCl	27,800	28,100	. . . . .	33,800	31,600	(30,300)	0.93	0.82	. . . . .
CuBr	. . . . .	23,700	. . . . .	. . .	25,000	(23,700)	1.00	0.95	. . . . .
CuI	. . . . .	16,600	. . . . .	. . .	. . . . .	16,600	1.00	1.00	. . . . .
TlCl	43,200	43,500	43,700	48,300	46,100	(44,800)	0.97	0.89	1.39×10^{-3}
TlBr	. . . . .	39,600	39,700	. . .	41,300	(40,000)	0.99	0.96	1.64×10^{-3}
TlI	. . . . .	. . . .	29,900	. . .	. . . . .	30,200	0.99	0.99	1.92×10^{-4}
Hg_2Cl_2	49,400	50,000	52,100	62,000	57,600	(55,000) [3] (53,800) [4] (46,400) [5]	0.93	0.80	1.6×10^{-6}
Hg_2Br_2	. . . . .	42,800	42,900	. . .	49,000 [3]	(45,200) [4] 28,800 [3]	0.95	0.88	1.4×10^{-7} [2]
Hg_2I_2	. . . . .	26,800	[46,400]	. . .	. . . . .	(27,600) [4] (45,600) [5]	0.97	0.93	6.1×10^{-10} [2]
$HgCl_2$	. . . . .	43,200 [5]	42,600	52,600	48,200 [3]	(45,000) [4] (37,900) [5]	0.96	0.81	5.26×10^{-1} [2]
$HgBr_2$	. . . . .	. . . . .	37,300	. . .	40,500 [3]	(37,300) [4] 25,100 [3]	1.00	0.92	3.4×10^{-2} [2]
HgI_2 (red)	. . . . .	. . . . .	24,100	. . .	. . . . .	(24,500) [4]	0.98	0.96	2.6×10^{-4} [2]
$PbCl_2$	74,800	75,400	74,300	82,700	78,300	(75,700)	1.00	0.90	7.14×10^{-2}
$PbBr_2$	. . . . .	64,200	62,300	. . .	64,500	(61,900)	1.04	1.00	4.64×10^{-2}
PbI_2	. . . . .	41,700	42,300	. . .	. . . . .	39,800	1.05	1.05	2.98×10^{-3}

[1] Berthlot's value.
[2] At 25°.
[3] Computed from column 4.
[4] Using Lewis' recent determination of the electrolytic potential of silver, the values for the chloride, bromide and iodide are 26,500, 23,300 and [27,000]. (See J. Am. Chem. Soc. 28, 158 (1906).
[5] Mercury liquid.
[6] Mercury solid.

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Tables. Column 5 contains the total energy of the chlorides with respect to gaseous chlorine. From this value, the heat of vaporization of chlorine (2,200 cal. for one atomic weight[16]) has been subtracted, and the so-obtained total energies referred to liquid chlorine are given in column 6, as are also the total energies of the bromide referred to liquid bromine. Column 7 contains the total energies referred to the halogens as solids. In the case of the bromides, the heat of fusion of bromine at its melting point —7.3° (1,300 cal.) has been subtracted from the value given in column 7 to get the total energy referred to solid bromine. The heat of fusion of chlorine has not been determined, but as an approximate basis of comparison, the heat of fusion has been assumed identical with that of bromine, which seems justifiable, since bromine and chlorine differ but little. These values are of course fictitious ones, since solid chlorine and bromine cannot exist at 18°; they are therefore enclosed in parentheses. They represent what the total energies would be if the solid elements were superheated to 18°, and there had the same heat of fusion as at lower temperatures. In the case of mercury halides, the total energy is given in the seventh column with respect both to solid and to liquid mercury, the heat of fusion (600 cal.) being assumed identical with that at the melting point.

Column 8 contains the ratio of the free to the total energies referred to the elements in the solid state, while column 9 gives the same ratio for the elements in the ordinary state. (For the chlorides this is the ratio of values in column 2 to those in column 5.) Column 10 gives the values of the solubilities used in computing column 4.

All energy values are gram-calories, are for one formula weight of salt as shown in the first column, and are based on the convention that the energy of the elements (considered gaseous, liquid or solid, as shown) is zero. The chlorine when gaseous is at atmospheric pressure.

Table VI contains the results for other compounds than the halides, and needs no explanation.

[16] It is not clear whether this value, which is cited as a private communication from Knietsch includes the external work; but this would make a difference of only about 300 cal.

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TABLE VI.

THE FREE AND TOTAL ENERGIES OF THE OXIDES OF SILVER AND MERCURY, OF WATER, AMMONIA AND HYDROCHLORIC ACID AT ABOUT 18°.

Compound.	Free Energy × (−1)	Total Energy × (−1)	Ratio of Free to Total Energy.
Hg_2O	13400	22200	0.60
Ag_2O [1]	3900	5900	0.66
H_2O (liq)	55500	67600	0.82
H_2O [2]	53800	57500	0.93
HCl [2]	22300	22200	1.01
HBr_2	11950	8400	1.4
NH_3 [2] (Baur)	45200	11400	4.00
NH_3 [2] (Haber)	5100	11400	0.45

DISCUSSION OF THE RESULTS.

First may be noted the good agreement between the free energy values of column 2 or 3 and those of column 4 in table V, the differences between which seldom exceed 4 per cent. The two series of values are based upon independent data, except that the same measurements of potentials of the halogen electrodes against halide solutions are, to a great extent, involved in both calculations. Except with respect to this last factor, the agreement is therefore a confirmation of the accuracy of the results. To this agreement there are two pronounced exceptions, namely, in the case of the iodides of silver and mercurous mercury, where the free energies calculated from solubilities and electrolytic potentials against normal solutions of the ions exceed those calculated from the electromotive force of cells with the salts present as solid phases by 65 and 73 per cent. The explanation of this extraordinary disagreement is by no means obvious. It cannot be due to an error in the electrolytic potential of the iodine electrode, for this is in substance common to both calculations, nor to one in that of the silver or mercury electrode, for this would have produced disagreement also in the cases of the chlorides and bromides of these elements; it is, moreover,

[1] The free energy computed from Lewis' recent value of the decomposition pressure of silver oxide is—3,310 cal. [See J. Am. Chem. Soc, *28*, 158 (1906)].

[2] Compounds gaseous at atmospheric pressure. In the case of water this condition is of course unrealizable at 18°, but the computed values represent nevertheless approximately what the energies would be if water vapor were supersaturated to that extent.

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difficult to believe it is due to an error in the potentials of the metals against the saturated solutions, since these values are based on fairly concordant measurements by different observers—five in the case of silver iodide, two in the case of mercurous iodide; and finally, it can hardly be due to error in the solubilities, for in order to give values of the free energy identical with those computed from the potentials against the saturated solutions, it would be necessary to assume for these two iodides solubilities (1.1×10^{-4} for AgI, 7.8×10^{-5} for Hg_2I_2) greater than those for the corresponding chlorides (1.06×10^{-5} for AgCl, 1.6×10^{-6} for Hg_2Cl_2) which is well known not to be the case. The most probable explanation of the discrepancy would seem to be that there exists in the solutions of these iodides complex ions, which make the computation from their solubilities uncertain. However this may be, from every point of view the free energy computed in the other way seems more reliable; first, because it does not involve any theoretical assumptions; second, because its values correspond for these two salts far better with those of the total energy (see below); and third, because they fall in line with those for the corresponding chlorides and bromides. Another point worthy of mention in connection with the two sets of free energy values is that in case of mercurous chloride and bromide, these agree more closely when the salts are assumed to be tri-ionic ones of the formula $(Hg_2)Cl_2$ or $(Hg_2)Br_2$ rather than di-ionic ones of the formula HgCl or HgBr. Thus, the values calculated from the solubilities under the former assumption are (as given in the table) 52,100 for the chloride, 42,900 calories for the bromide, and under the latter assumption, 60,600 and 53,400 calories respectively, while the values computed from the potentials against the saturated solutions are 49,400 and 42,800 calories respectively.

In regard to the magnitude of the free energies of the different compounds, the following approximate regularities will be seen to exist: (1) In the case of these solid halides, the chloride has a free energy uniformly greater than that of the corresponding bromide by from 2,500 to 5,500 calories per equivalent, and the bromide has a free energy greater than that of the corresponding iodide by 7,000 to 11,000 calories per equivalent.

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(2) The corresponding halides of mercurous mercury, silver, and cuprous copper have free energies which differ from each other by less than 3,500 calories per equivalent, but which increase slightly in every case in the order, mercury, silver, and copper.[17]

The most important general conclusion to be drawn from these results relates, however, to the connection between the free and total energies. It will be seen from column 8 of table V, that *the ratio of the free to the total energy of these solid salts when these energies are referred to, those of the elements in the solid state as zero do not differ from unity by more than 7 per cent.,* except in the single instance of silver iodide. This principle, which is of great importance, since it enables for approximate purposes the usually well-known heat of formation to be employed in the place of the often unknown free energy in the study of the equilibrium of reactions involving solid substances, previously had not been so extensively tested and confirmed.

An examination of the last three rows of values in Table VI shows that for gaseous water and hydrochloric acid, produced out of the gaseous elements, the ratio of free to total energy is not far from unity, but that for hydrobromic acid and ammonia the discrepancy is great, showing the absence of a simple relation.

The author here wishes to express his very sincere thanks to Professor A. A. Noyes for the valuable advice received while carrying out this work, without which it would not have arrived at its present state.

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DISCUSSION.

DR. J. W. RICHARDS: I cannot agree with the statement that this free energy decrease is a vastly more important quantity than the heat evolved by the reaction. In almost all industrial opera-

[17] This will be more obvious from the following summary of the free energies per equivalent of salt:

	Cl.	Diff.	Br.	Diff.	I.	Diff.
Hg (ous)	24,700		21,400		13,400	
Ag	25,600	900	23,000	1,600	15,900	2,500
Cu (ous)	28,100	2,500	23,700	700	16,600	900

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tions where the importance of chemistry is largely acknowledged, I think the heat which is evolved in the reaction is a measure of the work which it requires to produce the reaction, and is a measure of the energy which is obtained from the reaction. It may be that in certain electromotive forces of batteries this is a more important quantity; but the author has not limited his statement to that special case. We have seen the formulae arranged in the order from one where there is no doubt as to what the reactions are, to those where there is considerable; and while I will admit that there are, according to my views, very considerable doubts as to the accuracy of these later measurements in which there are so many assumptions which may be or may not be true, I also think that the very first reaction, in which there is presumed to be no doubt, is one where there is an extreme amount of doubt as to its representing what it is said to represent. I cannot assume that that reaction represents the heat of formation of water or the free energy decrease from the elements hydrogen and oxygen, unless there is absolutely no heat of combination or of union of hydrogen and oxygen with platinum. All my training is the other way; to regard that even if hydrogen was only occluded in the platinum or oxygen occluded in the platinum, that there is some heat of condensation, and that it would be wrong to regard hydrogen and oxygen on the platinum electrodes as being the equivalents of free hydrogen and free oxygen. I think, therefore, there is a very considerable doubt as to the author's interpretation of the first reaction, not to speak of the later ones.

PROF. W. LASH MILLER: I suppose that, having read the paper in behalf of the author, I am the one to reply. In the first place, then, as to the importance of the free energy; this naturally depends on the point of view. If one wishes to be able to predict what reactions may take place, and what cannot take place, when given reagents are brought together, the free energy is of the very greatest importance; on the other hand, if the object is to calculate the amount of heat set free during a given reaction, the total energy is the important function.

The second matter dealt with, was the evolution of heat when oxygen is absorbed by platinum. In the experiments on which Mr. Thompson's calculations are based, oxygen and hydrogen gases were converted into water, reversibly, under conditions

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which enabled him to calculate the amount of work to be gained from the reaction; and the amount of work so gained per molecule of water formed, is what the author calls the (negative) free energy of water. The compound (or whatever it is) of platinum and oxygen may be looked upon as merely part of the apparatus, for like the beakers and the wires it is left altogether unchanged in quantity and composition at the end of the measurement. During the course of the experiment, no doubt, the platinum keeps continually absorbing fresh oxygen, but only to replace that lost to the solution in the cell; for every gram of oxygen absorbed, a gram is given off, so that the evolution of heat due to the formation of the oxygen compound is just balanced by the absorption of heat due to its decomposition, and the net result is the same as though both were zero.

PRESIDENT BANCROFT: Did I understand Mr. Richards to imply that the heat of reaction is an accurate measure of the work if the reaction occurs in the factory, while it is not an accurate measure of the work if it takes place in the laboratory?

DR. RICHARDS: I was speaking of the commercial application of these quantities of heat and that the heat of the reaction—the total heat—was the important thing from the metallurgical and chemical standpoint, as to the energy required to produce the reaction.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

ELECTROLYSIS OF CAUSTIC SODA.

By Joseph W. Richards.

At the present time, all metallic sodium commercially produced is made by the electrolysis of caustic soda, and it has seemed an opportune time to review the history of the electrolysis of this salt, and so see what information exists upon the theory and practice of this process.

Sir Humphrey Davy opened up the subject in his historical Bakerian Lecture, delivered before the Royal Society on November 19, 1807, and printed in full in the "Philosophical Transactions" for 1808. The following extracts from this paper will set forth the main outlines of this great chemical discovery.

"In the course of a laborious experimental application of the powers of electrochemical analysis, to bodies which have appeared simple when examined by common chemical agents, or which, at least, have never been decomposed, it has been my good fortune to obtain new and singular results."

"I have tried several experiments in the electrization of potash rendered fluid by heat, with the hope of being able to collect the combustible matter, but without success; and I only attained my object, by employing electricity as the common agent for fusion and decomposition."

"A small piece of pure potash, which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4, in a state of intense activity; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. The whole apparatus was in the open atmosphere."

"Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid; but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces."

"Soda, when acted upon in the same manner as potash, exhibited an analogous result; but the decomposition demanded greater intensity of action in the batteries, or the alkali was required to be in much thinner and smaller pieces."

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"It appears then, that in these facts there is the same evidence for the decomposition of potash and soda into oxygen and two peculiar substances, as there is for the decomposition of sulphuric and phosphoric acids and the metallic oxides into oxygene and their respective combustible bases."

"Though, in the explanation of the various results of experiments that have been detailed, the antiphlogistic solution of the phenomena has been uniformly adopted, yet the motive for employing it has been rather a sense of its beauty and precision, than a conviction of its permanency and truth."

As far as the writer can discern, Davy thought he had decomposed fused caustic soda into oxygen and sodium, and apparently did not observe any evolution of hydrogen, either alone at the cathode or as water vapor at the anode, and so concluded that caustic soda was sodium oxide.

G. Janeczek,[1] of Prague, in 1875, was the first to maintain that caustic soda was decomposed electrolytically into Na at the cathode and OH at the anode, where the latter forms oxygen and water vapor; any hydrogen liberated at the cathode is set free by the reaction of metallic sodium upon the fused caustic.

In 1890, Mr. H. Y. Castner solved the problem of the industrial electrolysis of fused caustic soda (United States patent, 452,030, of May 12, 1891, which expires May 12, 1908). The patent papers describe the basis of the process as the discovery that caustic soda furnishes sodium in practicable quantities only when electrolyzed between its melting point (310° C.) and a temperature 20° higher; that above 330°, no appreciable quantity of sodium is obtained. The reasons for this are vaguely stated to be that as the temperature rises, the electrolyte absorbs both sodium and oxygen, so that at a certain temperature the products are absorbed as quickly as they can be separated, and no sodium is obtained. Regarding the electrolysis at proper low temperatures, Castner stated that the water in the caustic soda is decomposed into oxygen, appearing at the cathode, resulting, altogether, in the evolution of oxygen, or of a mixture of oxygen and water vapor, at the anode, while sodium and hydrogen, or sodium alone, is evolved at the cathode.

As far as apparatus is concerned, Castner devised a very practical form, in which the circular iron cathode was surmounted by a cylinder of metal gauze to prevent the sodium globules

[1] Berichte der Deutschen Chemische Gesellschaft, p. 1018 (1875).

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from flying over to the anode, and there being oxidized. The Castner patent covers both the process and the apparatus.

Rathenau and Suter[2] patented a method of electrolyzing fused caustic soda, which was in use for some time at the works of the Aluminum Industrial Aktien Gesellschaft at Neuhausen, Switzerland. The distinguishing feature of this was the use of an external cooled cathode, the high current density of 1,000 amperes per square decimeter, and the withdrawing of the sodium out of the bath as soon as it was formed, as calcium is now being made. The electrochemical works at Bitlerfield are said to have also used this apparatus since 1895. The patent claims read:

(1) An apparatus for the electrolytic separation of alkaline and alkaline earth metals from melted electrolytes, having negative electrodes of vertical rods or shoes with small active surface entirely outside the melt, and touching the same only by capillary contact at the surface, so that the metal separated out is accessible from all sides and floats on the surface.

(2) The arrangement of "touching electrodes" so that they are free to move away from the surface they touch, to facilitate removal of the metal during the operation.

Le Blanc and Brode made a long investigation, which is reported in "Zeitsch. für Electrochemie," September 11, 1902, and from which we take the following:

"We now know surely, that when electrolysing melted NaOH, oxygen and water vapor are evolved at the anode, the latter diffusing in the melt and reacting on the sodium separated at the cathode, evolves hydrogen. Since for two equivalents of sodium separated one equivalent of water is formed, it follows that the highest output of the Castner process is 50 per cent.; it seldom exceeds 40 per cent."

"Electrolysing a melt containing sodium in excess, at 350° to 360°, the first evolution of gas at the anode occurs at 2.4 volts electrode-potential; at 400° to 420° no gas evolution was visible at 2.5 volts. The depolarising action of dissolved sodium was so great at these temperatures that oxygen could evolve at the anode only at high current densities. The gas then evolving is detonating gas mixed with oxygen. When the apparatus is too hot, the melt dissolves too much sodium, which partly depolarises the anode and partly reacts upon the water there formed, producing large quantities of detonating gas, which explode. At lower temperatures, in consequence of the diminished solubility, both these reactions attain a minimum, and the hydrogen evolution takes place almost entirely within the cathode net. We have here the paradox, that at high temperatures hydrogen is evolved at the anode, at low temperatures at the anode."

"Whether anodic evolution of gas will be visible at a certain high temperature, depends on the current density."

[2] Zeitschrift für Elektrochemie (1898), p. 44, 369; 7, 252 (1900).

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"The reactions proceed similarly, when, as in large scale working, excess of sodium is always present around the cathode. The cessation of evolution of gas at the anode is then not a result of the increased capability of the melt to dissolve oxygen gas, since in that case anodic hydrogen must still be liberated, but the consequence of the strong depolarising action of dissolved sodium, which unites with the free oxygen and water and prevents all evolution of gas."

"In the pure melted caustic soda, there is at the start no product present which can act depolarisingly (?) upon either anode or cathode, and so only small currents can pass with small applied voltage. But, superoxide forms at the anode and dissolved sodium at the cathode, which at the beginning react upon each other largely to Na^2O.

$$Na^2O^2 + 2Na = 2Na^2O$$

The latter unites with the water liberated at the anode to form 2NaOH. Besides, part of the sodium will react directly upon the H^2O. Finally, one secondary electrode reaction overpowers the other, resulting in a melt saturated with either Na or Na^2O^2. We can artificially regulate this also by circulating the melt towards the cathode or *vice versa.*"

"If the water formed at the anode can be kept from getting to the cathode, or the sodium dissolved at the cathode from getting to the anode, the efficiency can be increased. This should be attainable by using a suitable diaphragm, while a current of well-dried air passed through the anode melt would remove its water."

Le Blanc and Brode's conclusions may be summarized as follows:

1. Melted caustic soda containing water shows two decomposition voltages, 1.3 and 2.2 volts. When the melt is free from water, the lower point disappears.

2. By the quantitative analysis of the gases evolved, it is shown that both decomposition voltages have a real significance; at 1.3 volts, hydrogen and oxygen are evolved; at 2.2 volts, sodium and oxygen. The output of oxygen is not quantitative, but increases with the current density. The evolution of hydrogen, so long as no free sodium appears, is below 2.2 volts. A melt containing no water gives above 2.2 volts only sodium, and no hydrogen.

3. Melted caustic rapidly comes into equilibrium with the vapor tension of the surrounding air, so that under ordinary conditions, it contains a noticeable water content. Completely de-hydrated caustic is therefore exceedingly hygroscopic.

4. Fused caustic containing free sodium, gives on electrolysis (with high current densities) both oxygen and water at the anode, which is only to be explained by the evolution there of OH.

5. The gases evolving in the Castner apparatus are, first, hydrogen at the cathode, and oxygen, water, and, finally,

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detonating gas at the anode. The latter causes the explosions which take place, which occur in spite of using a diaphragm and keeping anodic and cathodic products separate by diaphragms of metallic netting. The fear of such explosions has limited the size of the apparatus, so far constructed, from 1,000 to 1,250 amperes.

H. Becker uses an apparatus very similar in general arrangement to the Castner, with a particularly designed hood or cover above the cathode to collect and protect the ascending sodium. The electrolyte contains caustic soda and carbonate, and both these salts are to be added during electrolysis, while no explosions are said to occur. These statements have been investigated at length by one of our members, Mr. Carrier,[3] who found that only the caustic was decomposed, and, therefore, that an equivalent amount of caustic must be added. The only advantage remaining would be freedom from explosions.

E. A. Ashcroft[4] discharges lead-sodium alloy, as anode, in fused caustic soda, and collects the sodium thereof at the cathode. He states in his patent that the transfer takes place quite smoothly, the OH liberated at the anode being entirely absorbed in reforming NaOH, while sodium alone, and no hydrogen gas, is obtained at the cathode. This is electrolysis under very different conditions from the decomposition of caustic, since no decomposition voltage is absorbed, and it would be very interesting to know the behavior of this reaction at temperatures where sodium is supposed to actively redissolve.

G. P. Scholl (United States patent, 679,997) electrolyses a mixture of equal parts of caustic soda and sodium sulphide, using a low tension current. The idea is to decompose the sulphide present into sodium and sulphur, the latter being supposed to react upon the caustic soda present, and thus to reform Na^2S without any assistance from the current. There is some doubt about what reaction takes place in this electrolyte; at the beginning, very little gas is evolved at the anode and a great deal at the cathode; subsequently, sodium appears at the cathode, and then gas appears only, and freely, at the anode. There is no sulphur vapor or sulphur oxide evolved, and there is an

[3] Electrochemical Industry, September, 1904.
[4] Trans. Am. Electrochemical Soc., Vol. IX.

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almost total absence of the detonations which are so annoying when electrolyzing caustic soda alone. The bath is regenerated by adding fresh caustic; but it is almost certain that sulphate of soda forms and accumulates in the melt until it interferes with the fusibility of the bath. This process deserves an extended scientific investigation, which has, so far, not been made, or, if made, has not as yet been published.

The whole subject of the electrolysis of caustic soda needs further investigation. It needs to be shown what form the sodium takes when it redissolves in the melt at over 20° above the melting point; what form the oxygen takes when it is evolved in less than the theoretical quantity; whether hydrogen can be continuously evolved from the bath by a low current until only sodium oxide remains in it; whether it may not be possible to intercept the water vapor formed at the anode and (possibly by maintaining an intermediate part of the bath at a higher temperature and traversing it by a current of dried air) thus make it possible to obtain much greater efficiency of separation of sodium, for the amperes passing; whether explosions of detonating gas evolved at the anode cannot be avoided by use of an oxidizable anode which would not contaminate the bath. There is also a wide field for theoretical and practical, laboratory and workshop study of this problem.

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DISCUSSION.

DR. FORSSELL: Once, when making up a solution of pure sodium hydrate, I did it by placing a silver dish with pieces of metallic sodium in the upper part of a desiccator, filling water in the space below, thus making the water distill over to the sodium gradually. The following morning I noted that pieces of the sodium were floating in the solution formed. To determine whether the failure of a reaction might be due to formation of a protecting crust, I cut a piece under the solution. No action took place, however, and the surface of the metal remained bright

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for some time. It seems, therefore, as if an equilibrium had been attained in the system formed.

From this observation it does not appear impossible that an electro deposition of metallic sodium from an aqueous solution of sodium hydrate of this concentration may be accomplished at low temperatures.

PRESIDENT BANCROFT: That certainly is a very interesting phenomenon, which deserves able and very careful study.

MR. H. E. PATTEN: I would like to say that it is my remembrance that we had that same point up in the Wisconsin Laboratory. Prof. Kahlenberg was able, I believe, to put sodium in contact with very strong caustic soda solution and not get it acted upon.

DR. C. S. PALMER: Was the action carried on by fused sodium hydrate?

MR. PATTEN: I remember at the time that the possibility of depositing sodium was suggested there. That you could make such a strong solution of caustic soda in water that the metallic sodium immersed therein would not be acted upon. In general the plating of a metal from a solution is controlled by the *rate* of deposition.

PRESIDENT BANCROFT: Having gone so far as that, it seems rather a pity that the actual proof should not have been given by depositing metallic sodium from an aqueous solution at room temperature.

MR. CARVETH: In these experiments as observed by Mr. Forssell, may not the sodium have been coated by metallic peroxide which prevented its being reacted on by the caustic soda?

MR. PATTEN: I would not say but what that is possible. I am simply stating the fact that you get to a point in the concentration of caustic soda where the metallic sodium is not acted upon. If you take sodium and let it act upon amyl alcohol, you will have a similar case. I believe Mr. Mott and I mentioned in a paper on lithium chloride in alcohols, that if you take lithium or sodium in amyl alcohol you get to a point where the reaction evolving hydrogen is extremely slow and the surface of the metal appears to be bright.

MR. FORSSELL: I noticed the surface stayed the same a long time and the sodium was not changed into a sodium solution.

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DR. J. W. RICHARDS: In connection with a previous remark, I wish to say that sodium has been plated out of a very concentrated caustic soda solution as metallic sodium at ordinary temperatures. I have not the reference now; but I think that Davy did it some years after having first produced the metal.

MR. PATTEN: The same thing would apply to that little abstract published some years ago in regard to the deposition of calcium from a solution of calcium chloride in alcohol, with enough water added to redissolve the coating of calcium oxide which is formed. Now that deposit comes out at such extremely high current density that it was not thought possible, at the time, to analyze the material; if you get that deposit on a very fine platinum wire and quickly put it into water, you get a large evolution of hydrogen, that is out of all proportion to the gas which we know is given off when lime acts upon water; so it seems to me that the same thing holds true with regard to calcium as holds for sodium.

MR. C. F. CARRIER, JR.: The electrolysis of sodium hydroxide seems to yield sodium at the cathode and hydroxyl groups at the anode, for LeBlanc and Brode have proved the formation of water as well as oxygen at the anode, probably formed by the breaking down of two hydroxyl groups: $OH + OH = H_2O + O$. The primary action in the Castner cell seems to be the decomposition of water, for on starting the electrolysis nothing but O and H is obtained. In practice the bath is never free from water, for even if made anhydrous by the addition of metallic sodium, the passage of the current forms water as shown above. If then water is decomposed at a lower voltage than NaOH, it would seem that the liberation of sodium only takes place when there are not sufficient H ions to carry the current, or in other words, the current used is more than sufficient to decompose all of the water formed at the anode.

As the temperature rises the liberation of sodium ceases and finally there is no production of gases either. If sodium hydroxide is electrolysed at a full red heat (700°-800°) with a soluble anode of lead-sodium alloy, the electrolyte remains perfectly quiet, no gases or sodium being liberated during a run of nearly two hours with a current of 800 amperes.

At temperatures more than 20° above the melting point of

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NaOH, it is quite probable that both the anode and cathode products react with the electrolyte forming products which would depolarize the other electrode, but such temperature conditions do not hold in the Castner cell. If the metallic sodium fog, as suggested by Lorenz, can reach the anode, it will form peroxide and this in turn will depolarize the cathode.

The explosions in the Castner cell may be due to bi-polar electrode effects. The speaker observed that in an experimental apparatus there were no further explosions after the metal screen was removed.

The speaker is inclined to the opinion that the loss of ampere efficiency in the electrolysis of NaOH is due first to the necessity of electrolytically decomposing all water formed at the anode, and further to some depolarizing action the exact nature of which has not been fully demonstrated.

MR. TOWNSEND: I may state that in electrolyzing sodium chloride with very high current density in a cell in which the cathode is in contact with a mineral oil, I have noticed at times a flocculent deposit on the cathode which floats off into the oil and may be collected in small amounts. This I presume to contain sodium, since it evolves hydrogen with water and yields an alkaline solution.

PRESIDENT BANCROFT: Is this sodium set free from an aqueous solution of sodium chlorid?

MR. TOWNSEND: Yes. By increasing the current density and decreasing the percolation the concentration of caustic soda may be carried to the saturation point. Under these conditions sodium may be deposited faster than the strong caustic solution can oxidize it, in which case the flocculent deposit appears. The situation is practically the same as when a highly concentrated solution of caustic soda is electrolyzed without a diaphragm.

MR. A. E. ASHCROFT: I don't think there is anything so very surprising in the fact that you get metallic sodium in the presence of water. It is merely a question of the balance of affinities, so to speak. As a matter of fact any caustic solution has a very strong affinity for water; and it is very easy to conceive that the point may arise when the affinity of water for the solution is actually as great as for the metal, because we know the same thing happens with strong sulphuric acid and zinc, etc. As

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a matter of fact I have verified the experiment referred to myself. but it is also a question of the time factor in the case of sodium and caustic solution.

Passing on to the other parts of Dr. Richards' very interesting paper, there is one point whereon I think I might add a little bit to the information; that is in the work which Dr. Roseben and staff of the United Alkali Company have done on the Ashcroft sodium process quite a lot of work on caustic has been done and one particular point enunciated lately was that in the electrolysis of caustic soda under the conditions of a soluble anode, when the temperature rises, absorption of sodium takes place in caustic soda practically as if it were a pure solution of the metal; but when you work out the reactions there is very good proof that there is a formation of Na_4O. I cannot give you the reaction off hand.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

DIFFERENCES OF POTENTIAL BETWEEN MANGANESE AND LEAD PEROXIDES AND VARIOUS AQUEOUS AND NON-AQUEOUS SOLUTIONS.

By Louis Kahlenberg and Alonzo S. McDaniel.

The object of this work was to measure the differences of potential developed between electrodes of PbO_2 and MnO_2 and solutions in various non-aqueous solvents, and to compare these results with those found when water is substituted as solvent, all other factors remaining the same. The solvents used had to be such as would dissolve a solute also soluble in water and still yield solutions having a sufficient electrolytic conductivity for the purpose in hand. The solvents chosen were acetone, pyridine, amylamine and water. As LiCl is soluble in each of these liquids yielding conducting solutions, it was chosen as the solute.

The general plan of operation was to use one-eighth normal solutions of LiCl in acetone, pyridine and amyl amine, and also in mixtures of each of these solvents with varying amounts of water, the concentration of the solute remaining constant. In each experiment the one-eighth normal solution was chosen because LiCl is but slightly soluble in pyridine. The electrode was dipped into the solution, and the latter was connected with the Ostwald normal calomel electrode, and the combination measured. Thus the difference of potential between the peroxide electrode and the solution in question was determined, assuming for the normal calomel electrode the value —0.56 volts.

The peroxide electrodes were prepared by depositing the peroxides electrolytically upon anodes of platinum foil. The platinum strips employed were 0.5 cm. wide and 3 cm. long. Each was welded to a rather stiff piece of platinum wire. The surfaces of these platinum electrodes were carefully cleaned and scoured with sea sand, heated to redness in a Bunsen flame and coated with platinum black by electrolysis of an aqueous solution of platinic

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chloride. They were then thoroughly washed with distilled water and again heated to redness. This treatment always gave a clean, slightly roughened surface upon which a firmly adhering deposit of either PbO_2 or MnO_2 could be formed. The best results were obtained by repeated platinizing with subsequent heating until all the brightly polished surface of the platinum had completely disappeared. This insured a smooth, even deposit of peroxide which did not scale off and expose the platinum underneath, as generally happens when the deposit is formed upon bright platinum. PbO_2 was deposited upon the Pt, which served as anode, from a solution of lead nitrate acidified with sulphuric acid. The method of procedure then was much like that used by Tower in his studies on peroxide electrodes.[1] Care was taken not to get the coatings of the peroxides too thick, for it was found that electrodes with thinner coatings develop a constant E. M. F. in shorter time than those with a thicker deposit.

The pyridine employed was carefully dehydrated with fused caustic potash and redistilled, the fraction boiling at 114°-116° C. at 75.2 cm. pressure being taken. The amylamine was treated in like manner, and the fraction boiling between 97° and 100° was used. The acetone was dried with anhydrous copper sulphate and redistilled, a fraction boiling at 56° being employed. Distilled water was used in making up the aqueous solutions. The lithium chloride was prepared from the pure carbonate and hydrochloric acid, and was carefully dehydrated. In making up the solution in the non-aqueous solvents, special care was taken to avoid exposing the materials to the moisture in the air any more than absolutely necessary.

In making the measurements two principal difficulties were encountered. (1) Especially in most of the aqueous solutions the E. M. F. varied greatly with the time, and in some cases complete equilibrium was reached only after the electrodes were allowed to remain immersed in the solution for several days. (2) The task of making a suitable liquid contact between the calomel half cell and the non-aqueous solutions presented itself. The ordinary method using a connecting inverted U tube and intermediate vessel was objectionable in that the open vessels commonly used permitted the absorption of moisture from the air by the non-

[1] Zeit. Phys. Chem. *18*, 17 (1895).

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aqueous solutions. This factor was found to be of considerable consequence, for with open vessels no constant potentials could be obtained, the variations often being from 0.1 to 0.3 volts.

To prevent the absorption of moisture by the non-aqueous solutions, the usual method of making the connection was modified by closing the vessels by means of tightly fitting corks. The cork of the larger vessel into which the electrode dipped contained two holes, one for the admission of the electrode, the other for the limb of the U tube which connected this vessel with the smaller intermediate vessel. The cork of the latter also contained two holes for the admission of the tubes which joined it with the larger vessel and the calomel half cell, respectively. Before filling the vessels and the connecting U tube with the solution, all the parts were dried in an air bath and cooled in a desiccator. The two vessels were first filled with the solution and closed with corks. They were then fastened into proper position with respect to each other by clamps attached to small ring stands. The corks provided with the holes were placed in position on the connecting U tube. A very tightly fitting plug of dry filter paper was next inserted into one limb of the U tube, and a second similar plug was prepared ready for insertion into the other limb. The solution was then quickly poured into the U tube to the proper height and the second filter paper plug pushed into position. In this manner the U tube could be completely filled before the solution had time to soak through the filter plugs. It could then be inverted without losing any of the solution and placed in position so as to connect the two vessels. The corks attached to the U tubes could then be inserted tightly into their respective vessels. A piece of fused caustic potash was placed into the intermediate vessel when the non-aqueous solutions were measured, so that any moisture introduced by the tube which led to the half cell might be absorbed. The end of the latter tube was also closed by means of a filter paper plug. It could be raised and lowered at will through the hole in the stopper, and thus kept out of contact with the non-aqueous solution except during the short time required to make each measurement. With this arrangement it is difficult to see how any moisture could gain access to the solution into which the peroxide electrode dipped, even after standing for a considerable length of time.

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Indeed, the fact that concordant results were obtained only after this arrangement had been adopted would go to show that the solutions remained dry during the measurements.

Before dipping the electrodes into the non-aqueous solutions, they were dried in an air bath at 120° C. for several hours, and then cooled in a desiccator. To prevent the coating of peroxide from being scratched, the electrodes were protected by means of small bottomless test tubes. The wire attached to each electrode was passed through a small cork which was fitted into the test tube, thus holding the electrode in position. After drying and cooling, the electrodes were placed connected in pairs in U tubes filled with the solution in which they were to be measured, and allowed to remain so until equilibrium had become established before they were employed in the potential measurements. The electrodes were held in position in the closed U tubes by means of small corks which were pierced by the wires of the electrodes. In order to obtain check results two or more pairs of electrodes were used in making each series of measurements, except in a very few cases. Each pair was allowed to stand in the U tube a different length of time before the single potentials were measured in order to be sure that equilibrium had been reached. Very close agreement between the electrodes of each pair was always obtained, as is shown by the values in the accompanying tables. The discrepancies between the electrodes of the different pairs were not considerable except in some of the aqueous solutions. As a rule, a constant E. M. F. was reached more quickly in the non-aqueous than in the aqueous solutions, which fact is probably accounted for by the slow action of the water upon the peroxides to form hydrates.

The results obtained with one-eighth normal LiCl in non-aqueous solvents and in mixtures of these with water in various proportions are presented in the following Tables I to III. The headings of the vertical columns indicate the composition of the solvent used. The values for the different electrodes are tabulated horizontally, the results obtained from the different pairs of electrodes being grouped together. The figures given are the absolute single potentials in volts computed by subtracting from the total E. M. F. of each combination measured the value of the nor-

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mal calomel electrode, which was assumed to be —0.56 volt. In making such computation the sign of the potential difference was, of course, properly considered. For purposes of comparison the values obtained, using one-eighth normal aqueous H_2SO_4 solutions are also given in the last column in each table.

The time required for the electrodes to get into equilibrium with the solutions, (*i. e.*, the time necessary to reach a constant E. M. F.), varied. In the cases where the solvent consisted of pyridine, of pyridine plus water, of amylamine or amylamine plus water, the time required to secure a constant E. M. F. was from two to four hours; whereas when the solvent was acetone four to eight hours were necessary, and when the solvent was pure water or a mixture of acetone and water, one to two days were required to reach equilibrium.

In making the determinations the Poggendorff's compensation method was employed, a D'Arsonval galvanometer serving as zero instrument. The measurements were made to 0.001 volt at 20° C. A standard cadmium cell, the voltage of which was taken to be 1.0186 volts at 20° C. was used in making the comparisons. The E. M. F. of this standard cell was also checked by means of a Clark cell.

As a check the single potential of plain Pt was also measured; the results found are given in Table III.

TABLE I.

Single potentials in volts of MnO_2 and PbO_2 in $\frac{N}{8}$ Li Cl in pyridine and in pyridine plus water.

MnO_2					
Pyridine.	4 Vols. Pyridine + 1 Vol. Water.	1 Vol. Pyridine + 1 Vol. Water.	4 Vol. Water + 1 Vol. Pyridine	Water.	$\frac{N}{8}$ H_2SO_4 in Water.
—0.698	—0.758	—0.802	—0.866	—0 978	—1.566
—0.695	—0.758	—0.802	—0.866	—0.986	—1.565
—0.696	—0 766	—0.809	—0.862	—0.994	—1.562
—0.696	—0.766	—0.809	—0.862	—0.976	—1.568
PbO_2					
—0.838	—0.891	—0.945	—1.020	—1.196	—1.756
—0.836	—0 891	—0.945	—1.020	—1.200	—1.742
—0.842	—0 898	—0.943	—1.037	—1.192	—1.746
—0 842	—0.898	—0.943	—1.040	—1.189	—1.740

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TABLE II.

Single potentials in volts of MnO_2 and PbO_2 in $\frac{N}{8}$ Li Cl in acetone and in acetone plus water.

MnO_2

Acetone	4 Vol. Acetone + 1 Vol. Water.	1 Vol. Acetone + 1 Vol. Water.	4 Vol. Water + 1 Vol. Acetone.	Water.	$\frac{N}{8}$ H_2SO_4 in Water.
—1.137	—0.998	—0.996	—0.993	—0 978	—1.566
—1.137	—0 998	—0.996	—0.993	—0.986	—1.565
—1.121	—0.992	—0.984	—0.996	—0.994	—1.562
—1.121	—0.992	—0 984	—0.986	—0.976	—1.568

PbO_2

—1.328	—1.097	—1.105	—1.099	—1 196	—1.756
—1.328	—1.097	—1.105	—1.099	—1.200	—1.742
—1.346	—1.090	—1.094	—1.086	—1.192	—1.746
—1.346	—1.090	—1.094	—1.086	—1.189	—1.740

TABLE III.

Single potentials of MnO_2, PbO, and Pt in $\frac{N}{8}$ Li Cl in amylamine and in amylamine plus water.

MnO_2

Amyl amine.	2 vol. Amyl amine + 1 vol. Water.	1 vol. Amyl amine + 1 vol. Water.	1 vol. Amyl amine + 3 vol. Water.	1 vol. Amyl amine + 7 vol. Water.	2 vol Amyl amine + 25 vol. Water.	Water.	$\frac{N}{8}$ H_2SO_4 in Water.
—0 476	—0.472	—0.478	—0.498	—0.524	—0.534	—0.978	—1.566
—0.476	—0.472	—0.472	—0.503	—0.518	—0.530	—0.986	—1.565

PbO_2

—0.612	—0.700	—0.758	—0.765	—0.770	—0.776	—1.196	—1.756
—0.612	—0.696	—0.760	—0.763	—0.744	—0.780	—1.200	—1.742

Pt.

—0.402	—0.414			—0.456			
—0.402	—0.414			—0.456			

The results presented in Tables I to III are also represented graphically in Fig. 1. The data gathered with PbO_2 as the electrode are indicated by dotted line curves, and those obtained by employing MnO_2 are indicated by continuous line curves. The abscissas represent per cent. of water by volume and the ordinates the single potentials. The

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results are best discussed by reference to Fig. 1. It will be noted that in the case of each solvent and its mixtures with water the differences of potential for PbO_2 are greater than the corresponding values for MnO_2. In pure acetone as solvent the potential differences are higher than in water in case of both PbO_2 and MnO_2. Addition of 20 per cent. water causes a marked diminution in both cases. Further addition of water up to 80 per cent. produces practically no change in case of PbO_2, whereas in case of MnO_2 a very slight diminution in the potential occurs, which continues as more water is added to 100 per cent., while an addition of water to 100 per cent. in the PbO_2 case again causes an increase of difference of potential. The pyridine curves for both PbO_2 and MnO_2 are quite similar in character; they are also fairly regular in that a gradual increase of the amount of water

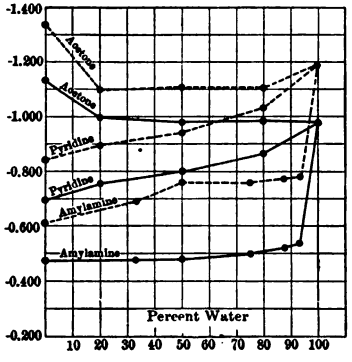

Fig. 1.

causes a gradual increase of potential difference in each case. The amylamine curves for PbO_2 and MnO_2 are also similar in that in the pure solvent the difference of potential is much below that in water, and that addition of water beyond 90 per cent. causes a great increase in the difference of potential in both cases. However, addition of water from 1 to 90 per cent. causes a greater increase in potential difference when PbO_2 is employed than when MnO_2 is used. Indeed, when the latter is employed the change of potential by addition of water up to 90 per cent. is remarkably slight. Indeed, the amylamine curves for the two peroxides are

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quite similar in character after 50 per cent. of water has been added to the solvent.

By referring to the last two columns of Tables I to III it will further be noted that when pure water is the solvent a remarkable increase in the negative character of the potential difference occurs when sulphuric acid is substituted for lithium chloride. The fact that the greatest differences of potential occur between the electrodes in question and acid solutions and much lower values are obtained when alkaline solutions—those containing pyridine and amylamine—are used, is evident from the results in the above tables. It is further clear that neutral solutions yield values falling between these extremes. This is also borne out by the data collected by Tower (l.c.) on aqueous solutions.

Tower developed a formula for computing the difference of potential between a MnO_2 electrode and a solution on the basis of Nernst's theory. This formula would explain qualitatively the extremes of difference of potential observed in acid and alkaline solutions, but later work by Tower[2], and especially by Smith[3], has shown that the formula does not give a satisfactory quantitative explanation of the values actually found even when only aqueous solutions are used. It is consequently unnecessary to dwell upon the matter further in this connection.

The results obtained indicate that the difference of potential between a peroxide electrode and the solution into which it dips is to be ascribed to the chemical affinity; *i. e.*, the chemical strain or potential, between electrode and liquid. Now the general chemical characteristics of PbO_2 and MnO_2 are well known. These substances are slightly acidic in character, and are strong oxidizing agents, moreover with water they slowly unite to form hydrates. The latter characteristic accounts for the fact that in aqueous solutions the E. M. F. produced by these electrodes does not readily become constant. With bases these oxides tend to unite to form salts, which would explain the less negative character of the potential difference developed in basic solutions. The values here recorded for pyridine solutions are, for example, of the same order of magnitude as those obtained for the stronger aqueous KOH solutions measured by Tower. Further, acids tend

[2] Zeit. Phys. Chem., *21*, 90 (1896).
[3] Ibid p. 93.

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to attack these peroxides with concomitant liberation of oxygen, which accounts for the much greater electronegative character of the potential difference in the acid solutions. Acetone is a neutral body, and rather an inert substance toward the peroxides as compared with such strong bases as pyridine and amylamine, or even as compared with a substance like water, so that the strong electronegative character of the potential developed in acetone—which is, however, below that developed in the acid solutions—can hardly be surprising. It would be of interest to study the differences of potential between peroxide electrodes and still other non-aqueous solutions, though such work consumes considerable time on account of the difficulties encountered, which have already been mentioned.

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DISCUSSION.

MR. W. C. ARSEM: I thought perhaps the strong electro-negative potential in the acetone might be due to the presence of acetic acid, which is very often found in acetone; or perhaps the formation of acetic acid from the acetone by the action of the metallic peroxides.

MR. PATTEN: I am sorry I cannot go into this research as well as I might have gone a year ago when Mr. McDaniel was doing the work next to me. He tested the solutions for acidity, I think. If Mr. Kahlenberg were here he could answer much better. The work was done with very great accuracy; I know they put a great deal of time on it and were very thorough in their work; so that I doubt if the acid played a part in this work. I will say, though, in reply to Mr. Arsem, that Freer's work upon the action of metals upon acetone shows that one of the hydrogens in acetone is actually replaceable. That would, to my mind, enter here, more than his statement in regard to the possible presence of acetic acid in the acetone. I submit that statement.

PROF. W. LASH MILLER: It occurs to me that in discussing

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the results of these experiments nothing has been said about what takes place where the non-aqueous solution comes in contact with the aqueous solution of the normal electrode. Very often the changes taking place at that point do not greatly affect the E. M. F., and they are always difficult to calculate; but in the present instances, where the passage of the current must involve the transfer of salts between aqueous solutions where they are very soluble, and other solutions where they are only slightly soluble, the expressions for the E. M. F. would contain terms involving the logarithms of the ratios of the solubilities, which might be fairly large, and might account in part for the different heights of the curves in Prof. Kahlenberg's figure. At all events it hardly seems safe to pass over this point without investigation.

PROF. KAHLENBERG: (*communicated*). With regard to the question raised by Mr. Arsem, it should be stated that the acetone solution used contained no acetic acid. Prof. Miller is quite right in calling attention to the fact that the E. M. F. at the junction of the non-aqueous and aqueous solutions was not separately determined. On account of the high resistance which many of the non-aqueous solutions have, it is very difficult to measure these small electromotive forces. In my opinion, they are so small that they do not influence the results materially.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

A NEW ELECTROLYTE FOR THE SILVER COULOMETER.

By Henry S. Carhart, H. H. Willard, and W. D. Henderson.

There are two inherent difficulties in the use of silver nitrate, as the electrolyte in a silver coulometer. They are: First, the looseness of the crystals on the cathode, which leads to loss, unless the precaution is taken to save and weigh the small amount washed off; and second, the supposed formation of a heavy anodic liquid, according to Professor T. W. Richards, which must be kept away from the cathode as completely as possible. The conference on electrical units of measurement, which was held at the Reichsanstalt last October, reaffirmed the definition of the international ampere in terms of the deposit of silver in a silver coulometer. Hence the necessity of pushing the inquiry further to ascertain if it is not possible to use another silver salt so as to eliminate one or both of the above difficulties presented by the electrolysis of silver nitrate. One of us (Mr. Willard) has accordingly devised a method of preparing the perchlorate of silver ($AgClO_4$) in a pure state in any desired quantity, and we have made a number of preliminary trials to determine its behavior as compared with silver nitrate in electrolysis. The work is only fairly begun, but the results thus far are so decidedly encouraging that we shall pursue the subject further in the immediate future.

Only a very few experiments have hitherto been made with other silver salts; and as these were not well chosen, they gave no better results than the nitrate. The ideal electrolyte would be one in which there is no change in composition during electrolysis. The first requisite, therefore, is that the salt employed shall be very stable, and that neither oxidation nor reduction products shall be formed during electrolysis; second, it should give a good adherent deposit; third, it must be readily soluble; fourth, it must be easily prepared in large quantity and in a state

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of purity. To exclude the possibility of the presence of more than two ions, the salt of a monobasic acid, which shows no tendency to form complex ions, should be chosen.

During an investigation on perchloric acid and its salts, the remarkable stability of the latter in aqueous solution suggested their use as electrolytes, and it appeared that silver perchlorate would be a better salt than the nitrate to use in the silver coulometer. Nitrates, for example, tend to form reduction products during electrolysis; perchlorates, on the other hand, form no reduction products, and electrolysis seems to cause no change whatever in their composition. Sulphates are also very stable, but silver sulphate is so difficultly soluble that only a 0.6 per cent. solution can be prepared at ordinary temperatures, and the low conductivity of such a dilute solution makes it undesirable. Silver perchlorate, however, is deliquescent and extremely soluble in water, so that solutions of any concentration may be prepared.

Preparation of Silver Perchlorate.

In order that this salt should have any practical value as an electrolyte, it was necessary to find a method of preparing it readily, for it is not on the market. The starting point in the preparation of perchlorates is sodium perchlorate, which is now obtainable, commercially, at a low price. It may be readily made in large quantities in the laboratory by the electrolysis of sodium chlorate.

A saturated solution of the perchlorate is prepared, diluted with about two and a half times its volume of hydrochloric acid (sp. gr. 1.20), and then saturated with the gas.[1] In this way, most of the sodium is precipitated as chloride, which may be filtered out through cloth. The solution of hydrochloric and perchloric acids is evaporated until heavy, white fumes of the latter appear. This expels all the hydrochloric, and leaves perchloric acid of about 60 per cent. strength, containing a little sodium perchlorate. To prepare the pure acid, the crude product is distilled, preferably in a vacuum, where no decomposition occurs. It can also be distilled under atmospheric pressure, but there is then a small loss, due to decomposition of a part of the acid

[1] This is similar to Kreider's method, Zeit. für Anorgan. Chem., 9, 342.

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into chlorine and its oxides, which dissolve in the distillate. They may be removed by aspirating air through the warm solution for several hours, leaving pure di-hydrated perchloric acid, containing about 73 per cent. acid. The hot acid, or its vapor, must not be allowed to come in contact with organic matter, and rubber connections are to be avoided as far as possible.

To prepare silver perchlorate, the oxide or carbonate could be dissolved in the acid; but the preparation of large quantities of these substances in a state of purity is troublesome and difficult. Since perchloric acid is much less volatile than nitric, it will displace the latter from its salts, and we may use silver nitrate directly. A suitable quantity of this salt is weighed out and an amount of perchloric acid slightly in excess of that theoretically required is added. The temperature is raised gradually until the nitrate has dissolved and nitric acid is freely evolved. Finally, the mass is maintained at 250° to 260° C. for several hours to remove the last traces of perchloric acid. A little chloride is almost invariably formed at this temperature; but if the salt is heated in a vacuum, a much lower temperature will suffice to remove the acid and no chloride will be formed. It is absolutely necessary to get a neutral product. The resulting salt is tested for nitrate by dropping a little into a solution of diphenylamine in concentrated sulphuric acid. No trace of blue color should appear. It is tested for neutrality by dissolving a little in water and adding blue litmus paper. For reasons that will appear later, it is impracticable to neutralize an excess of acid by adding silver oxide or carbonate. To make a solution, the silver perchlorate is dissolved in redistilled water, and any chloride present is filtered out.

Methods of Comparison.

In order that the results with the $AgClO_4$ might be compared with the best results hitherto obtained with $AgNO_3$, we prepared two coulometers of the pattern employed by Professor Guthe in his investigation at the Bureau of Standards. The porous cups were made from the same mould as his and at the same factory. The platinum vessels used as cathodes were ten centimetres in diameter and about five centimetres deep. Ten per cent. solutions of both salts were used in every case. The two

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coulometers were connected in series. After the deposition of from one to two or three grammes, with a current rarely in excess of 0.5 ampere, the platinum cups were carefully washed, left to soak in water over night, were then heated for four hours to a temperature of about 140°, and were finally transferred to desiccators to cool before weighing. The weighings were all made in the later comparisons by means of a large and very excellent Rüprecht balance as the chemical laboratory. In these same comparisons, the wash water was filtered through a small disc of filter paper in the bottom of a Gooch crucible. The paper was afterward ignited and the residue weighed.

Results.

First—The $AgClO_4$ used in the first six comparisons was neutralized with pure silver oxide or was prepared by treating carbonate of silver with perchloric acid. In all these cases, the perchlorate gave a distinctly heavier deposit than the nitrate, the difference amounting to more than one-tenth per cent. In this respect, therefore, the perchlorate agrees with the nitrate, since both give a heavier deposit with a solution neutralized with an oxide or a carbonate.

All the later experiments with the perchlorate were made with a solution of the salt made neutral without the use of either an oxide or a carbonate. Also distilled conductivity water was used to make the solutions.

Second—The deposit from the perchlorate differs markedly in appearance from that derived from the nitrate. In every case, whether the anode was in a porous cup resting on finely divided silver, as recommended by Guthe, or was enclosed in filter paper, the deposit was invariably in fine and very straight lines, running from the bottom of the platinum cup to the top of the solution. The deposit from the nitrate was as usual in more or less detached crystals, which do not adhere well together, as the deposit does when the electrolyte is the perchlorate. This conclusion has been confirmed in every case by the weighed silver washed out. It is always markedly greater when the silver is derived from the nitrate than when it comes from the perchlorate. From the latter, the silver washed out is often so small that it cannot be weighed.

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Moreover, if the platinum cups with the silver deposit are turned upside down on filter paper and lightly tapped, the one containing silver from the nitrate loses a shower of small crystals plainly visible to the unaided eye, while scarcely any at all can be seen on the other sheet.

When the perchlorate is used as the electrolyte, if the washing is carefully conducted, it is not necessary to save the washings and to weigh the residue, except when the object is to determine small residual differences that may result from varying the method of operation. The comparatively firm adherence of the deposit to the cathode, we consider a strong count in favor of the perchlorate of silver instead of the nitrate as the electrolyte in a silver coulometer.

The filter paper used in washing is Baker & Adamson's, washed in hydrochloric and hydrofluoric acids. The ash in one paper weighs 0.07 mg., and one of these papers makes at least twenty of the small discs used in the Gooch crucible.

Third—In most of the comparisons, the deposit from the perchlorate was heavier by an insignificant per cent. than that from the nitrate. This was true whether both anodes were in the porous cups, both wrapped in Baker & Adamson's washed filter paper, or one in a porous cup and the other in the filter paper. Three comparisons with both anodes wrapped in the filter paper gave a mean of 0.007 per cent. greater weight for the perchlorate. This difference is too small to be of any moment.

In two cases, when the anodes were enclosed in the filter paper, the deposit from the nitrate exceeded that from the perchlorate by 0.005 per cent. The differences were obtained by counterbalancing one platinum cup against the other, and correcting for the differences in the silver washed out.

In a few cases, comparisons were made between the porous cup and the filter paper, the electrolyte being the same in both coulometers, either the perchlorate or the nitrate. The deposit was invariably heavier in the coulometer with the porous cup. We are unable to reconcile these facts with the theory of a heavy anodic liquid, unless the filter paper we are using is a better porous diaphragm than our porous cups with the finely divided silver at the bottom. The use of a porous cup is objectionable from several points of view. It is not certain that it does not

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disintegrate to a slight extent, and thus add to the weight of the deposit by the minute particles that drop off. It always increases the electrical resistance and makes it variable, unless the precaution is taken to soak the cup in the electrolyte long enough to fill the pores before the current is turned on. The effect of the additional resistance is to increase the temperature of the electrolyte during the deposition, thus adding another element of uncertainty. The filter paper we use offers no appreciable resistance and does not disintegrate. Ordinary filter paper cannot be used. The impurities contained in it tend to give the deposited silver a faint yellowish tinge. We raise the question whether the effect of the filter paper itself on the amount of the deposit has been sufficiently investigated. We note that Professor Richards in his first paper on this subject found a difference between the porous cup coulometer and the filter paper coulometer of 0.08 per cent.; two years later he found 0.04 per cent.; and in the recent paper by Van Dijk, the difference is reduced to 0.025 per cent.

The investigation covered by this paper is to be regarded as preliminary only. It is our purpose to continue the research, particularly with reference to the constancy and reliability of the results with silver perchlorate. In pursuance of this purpose, it will be necessary to make several series of determinations for each set of conditions. Further, if it should be found that the proper choice of filter paper will avoid the necessity of using a porous cup, especially with the perchlorate as the electrolyte, a distinct advance will have been made.

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A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 3, 1906. President Bancroft in the Chair.

ERRORS IN PYROMETRY.

By E. S. Shepherd.

The last ten years has seen a marked advance in the perfection of pyrometric instruments, and, owing perhaps to the existence of several compact instruments which are now available, the use of the pyrometer among experimenters has been greatly increased. It is not the purpose of this paper to discuss the different forms of pyrometers, for this has been much better done elsewhere. If, however, the attention of those using such instruments can be called to a number of the common sources of error, it may result in a saving of considerable work, and therefore justify the paper.

The chemist is apt to have been spoiled for pyrometric work by the use of mercury thermometers, which, even in their poorest grades, give fairly accurate results; and as a result, he is apt to assume that the pyrometer can be used in the same haphazard fashion. This, unfortunately, is not the case. Take as an example the Seger cone method of determining melting points. Some investigators have thought to determine the melting points of mineral mixtures by moulding the minerals into the form of cones and heating them in a furnace alongside the Seger cone. This is all very well under certain conditions, and it is sometimes possible to obtain results which are approximately correct. But take for example the case of lime-silica mixtures, where the experimenter has mixed lime with silica, moulded it into a cone, and heated it in a furnace alongside a Seger cone. The result is, that at some temperature the lime and silica combine to form the silicate of calcium, and, in doing so, evolve a very appreciable quantity of heat, which necessarily raises the temperature of the experimental charge to one considerably higher than that of the Seger cone with which it is being compared. The temperature at which this combination

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takes place and the rate of reaction will depend, among other things, on the fineness of grinding and the intimacy of the mixture. Furthermore, all mixtures containing an eutectic along with a more refractory component, will be partially liquid after the eutectic melts, and may break down or stand up according as there is more or less of the eutectic present or the melted portion happens to be more or less viscous.

Owing to the difference in viscosity of mineral melts, it is by no means safe to compare the amount of "falling" of a mineral mixture with that of the Seger cone. There need be no relation whatsoever between them. Thus, albite will stand firmly in shape while passing from the solid to the amorphous state, and a Seger cone would not indicate anything like the true melting point. Furthermore, the *time factor* is therefore of the greatest importance in all such work.

Obviously, such a method will lead to erroneous conclusions; and if several examples of such careless work had not appeared recently, it would seem unnecessary to call attention to what is evidently an incorrect method.

Presumably, the platinum resistance thermometer is one of the most accurate means available for temperature up to 900° C.; but, as the size of the bulb is so great, it makes it very difficult to obtain a charge large enough to employ the full sensitiveness, with satisfactory results. This method also requires a number of very accurately calibrated boxes and leads. It follows, therefore, that for temperatures below 1,600° C., the thermocouple has come into very wide usage.

It is in the use of the thermocouple that one is most forcibly impressed with the way in which the chemists have translated their thermometer practice to pyrometry. For example, it has been held to be sufficient for the determination of the temperature, to insert the hot junction of the element into the bath, into the metal, or into a portion of the crucible, at some distance removed from the charge examined. In steel work, a hole is made in a steel block, and the element, sometimes protected by a wad of asbestos, but more frequently bare, is placed in the hole, and the temperatures carried up to 1,200 degrees, or more. The result of such practice is that the element becomes contaminated with iron and begins to read too low. In the cases which have come

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under my personal observation, the experimenters have failed to discover this fact, and have gone on, cheerfully assuming that the temperature registered on the scale of the galvanometer was necessarily the temperature of the substance investigated. The situation very closely resembles that of the mercurial thermometer used, in various households, for determining the out of doors temperature. The fact that the thermometer reads a given number of degrees is apt to be regarded as sufficient evidence that that is the temperature, and it is only with very great difficulty that we free ourselves from this idea, and learn that there may be different factors, different sources of error, in this high temperature work, from those which affect the readings of thermometers at ordinary temperatures. Somehow, the fact that we have a scale marked off in degrees seems to satisfy most of us that the markings on the scale really correspond to the indicated temperature. It may be asked how much of an error is introduced by neglecting such precaution, to which it can be replied that it frequently amounts to as much as 150°, due solely to the contamination of the element.

We have here taken no account of the fact that perhaps the galvanometer sticks and that the cold junctions of the wire may not be kept at constant temperature. This last feature is a very common error in such measurements. None of the commercial pyrometers make any arrangement for maintaining the cold junction constant, so that the temperature of this junction in actual practice may vary 1° to 20° from that for which the instrument was calibrated. In the absence of any adequate method of correcting for the temperature of the cold junction, it is easily seen that we have here a further error to add to the 150° mentioned above, due to the contamination of the element. One hundred and fifty degrees may be of no consequence in the running of commercial furnaces, but if the same apparatus is used for experimental investigation, of what value is the work? It is not believed that because an experiment is to be of *purely practical* value, one is justified in doing it in a careless, slipshod fashion. It is painfully evident that some investigators in that field which lies between pure science and pure practice, do not realize fully the importance of accuracy.

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Another source of error is that a high temperature can be maintained constant only over a very small space, and that, when an element is placed in a furnace, it does not necessarily follow that the temperature of the entire furnace is the temperature of the element. Only when an element and the material which is being investigated are placed in very intimate contact, can we be certain that we are getting the temperature of the substance in question. The variation in temperature of the ordinary electrical resistance furnace is apt to be from 10° to 50° in different parts of the furnace, and, in a gas furnace, the variation is much greater. It is necessary to use great care in setting up the apparatus before one can truly say that the material investigated was brought to a particular temperature. It is by no means permissible to place a thermo-element in one part of a graphite or metal block, the charge in another part, and then to say that the thermo-element gives the temperature of the charge. Nor is it a fair answer to say that such experiments are merely preliminary and that the difference in temperatures will be so slight as to be without effect on the result.

Not only do the metallurgists who investigate heat changes in steel, err in placing the element in contact with foreign metals, but there seems to be a general disregard of the fact that all hot metals have an appreciable vapor and that this vapor attacks the thermo-element, resulting in incorrect readings. If it were only that the element read low, the error would not be so serious, since it could be readily corrected by calibration, But for a great deal of this investigation, which involves determining heating and cooling curves, contamination of this sort just mentioned causes the element to lag in a way such that the reading will be higher or lower, depending on the rate at which the temperature is changing. Thermo-elements are always sensitive in reducing vapors and gases, so that the use of an unprotected or imperfectly protected element is certain to give erroneous results.

In the last two years, a paper has been published in which the author vigorously discusses whether or not a given heat effect occurred at 560 or 562½°, using an instrument which was calibrated to only 20° per millimeter; and while he no doubt could see that the needle of the galvanometer was not at an even

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division, it seems stretching the point to quarrel over the question whether it was 60, 62½, or 65°. The instrument used did not possess anything like the sensitiveness necessary to determine this point.

In recent years, a considerable amount of work has been done on the temperatures at which certain reactions occur, and, in this relation, a word of warning may not be out of place. The temperature at which a reaction begins is an indefinite one in nearly all cases. For example, take the temperature combinations between certain oxides which go to form minerals. It is found experimentally that combinations will occur over a range of temperatures, and that the time factor is a very important one. For example, lime and silica will combine slowly at 1,200°, more rapidly at 1,300°, and fairly rapidly at 1,400°; the melting point of this particular mixture was 1,512° C. It depends altogether upon how much time is given whether or not one would conclude that the reaction took place at any one of those temperatures. If the time is sufficiently short and the material coarsely ground or imperfectly mixed, the reaction would be less apparent than if the better conditions had been chosen. With coarsely ground materials, the inhomogeneity may give rise to entirely different reactions from those which represent equilibrium. It is commonly stated that the temperature of formation of a slag lies above its melting temperature, but this is only an accident of shop practice. If the materials are finely ground and intimately mixed, combination will occur below the temperature of fusion, and the observed phenomenon is due entirely to the coarseness of the materials, rendering combination difficult.

It is with reactions of this nature that a great many of the imperfect temperature observations are made. It may be that the observations are intended to be approximate only; but, after working over into the literature, somehow these approximations often come to have the status of accurately-established facts.

The use of the radiation pyrometer, which for a good deal of work has many advantages over the thermo-element, is also misleading in its simplicity. The person who buys an instrument of the usual type, and finds marked upon it a scale, so that by looking through the instrument and turning a few disks he comes out with a reading of so many degrees, is very apt to regard the

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temperature as determined with considerable accuracy. Of course, he may know better, but the fact that the scale says so many degrees seems to grow upon one until he is almost ready to swear that that is the temperature, although the makers of the instrument do not claim it, and his common sense shows him that the reading is only approximate. It is well known that in radiation pyrometry, the assumption is made that the radiation is "black." and it is also well known that in practical work, this condition of "blackness" is not easily attainable. It is therefore important that the person who is using an optical pyrometer make sure that the conditions of radiation approach as nearly to "blackness" as possible. As a matter of fact, in most commercial work, and where inexperienced persons are using these instruments, there is no pretense made of securing "black" radiation, and the errors of the reading in such cases may easily amount to 100° or 200°, or even more. In certain cases, where dense vapors are given off, it is folly to try to determine the temperature of the substance which is emitting the vapor. In carbon tube furnaces, for example, there is apt to be a carbon flame playing about the mouth or in the neck of the furnace, which may be several hundred degrees different in its temperature from that of the middle of the furnace. The temperature measured is that of the flame, not that of the furnace.

To sum up, the chief errors in pyrometry, in the hands of persons not specializing in this line of work, are due to the using of instruments under conditions in which they were not intended to be used. Then, too, the average person, who is in a hurry for results, is apt to take a reading under conditions which he realizes are not suitable for exact determination, but, after having obtained the reading, by some mysterious psychological process, to insist upon its accuracy. For the accurate determination of any of these points, it is absolutely necessary that the instruments be calibrated frequently with the same conditions as those under which they are used; and for the thermo-elements at least, it is of very great importance that the element be tested from time to time to see that it is in good condition, and that every care be taken to prevent its contamination by the metal vapors to which these elements are sensitive. We must come to

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realize more thoroughly that pyrometers are in no sense simple instruments which may be handled like thermometers. They have their own diseases and advantages, and call for great care in manipulation.

It is not for us to quarrel with the way in which commercial men use pyrometers—far from it; the more they use them and become accustomed to them, the better; but let us not take our *laboratory* practice from the commercial men, and then insist that ten or a hundred times greater accuracy has been secured, merely because the place where the experiment chanced to be performed was dignified by the name of laboratory.

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DISCUSSION.

MR F. F. SCHUETZ: I have been very much interested in Mr. Shepherd's paper on the "Errors of Pyrometry," and am glad to note that he dwells particularly upon the errors prevalent in the "thermo-electric" type of pyrometer.

The thermo-electric pyrometer is probably destined to be the most important form of pyrometer for temperature measurements up to 3,000° F. or 1,600° C., being capable of both indicating and recording temperatures, and adaptable to a great number and great variety of industrial applications. I think it is to this form of pyrometer that we should first lend our energies, striving to correct its errors and to perfect a commercial instrument which a person of ordinary intelligence may manipulate without having to take into consideration numerous conditions and factors which might affect the accuracy of his determinations—in fact, an instrument which eliminates the "personal equation."

The first error mentioned by Mr. Shepherd in connection with the thermo-electric pyrometer is that due to the contamination of the elements composing the couple through contact with the material into which it is inserted or through vapors given off from metals, etc., attacking said elements. I presume Mr. Shepherd has reference to the standard "Le Chatelier Couple," comprising elements of platinum and platinum with 10 per cent.

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of rhodium. Up to temperatures as high as 2,600° F., it is entirely unnecessary to employ these expensive elements. Much better results are obtained in using cheaper elements composed of such materials as nickel, steel, tungsten, copper, constantan, nickel-steel, German silver, etc. Couples formed of such materials have been found to give satisfactory results, especially if properly protected and insulated. A very convenient and efficient method of insulating and protecting thermo-electric couples is first to wind each element with asbestos thread and then to coat this with carborundum paint, using sodium silicate as a binder. For protection against temperatures of 2,000° F. and over, special tubes of nickel, plumbago, or porcelain are employed. For use in lead baths and the like, the asbestos-carborundum insulated couples may be further protected by an iron pipe welded together at the exposed end.

Another error mentioned is that due to the effect of variations of temperature at the cold end of the couple; and I should like to add— the "Resistance-Temperature Error," or error due to variations in the resistance of the system through temperature changes along the couple, leads, and the indicating instrument itself. Le Chatelier in a measure corrected for this error by concentrating considerable resistance at the indicating instrument, from 200 to 300 or more ohms being employed. This high resistance, however, necessitates the use of the delicate suspension galvanometer as an indicating instrument.

The "cold-end-temperature error" has usually been corrected by maintaining said cold end at constant temperature through the circulation of some liquid about it; or by placing it in melting ice. These methods are entirely unsuited for commercial applications and are usually dispensed with.

A very novel and ingenious method of overcoming and correcting these two errors has been recently devised by Prof. William H. Bristol, of the Stevens Institute of Technology. Prof. Bristol, in deliberate opposition to the orthodox and commonly-accepted views of Le Chatelier and others, employs a "low resistance system," the total resistance of which in no case exceeds ten ohms and in some instances is as low as four and one-half ohms. A much greater current is thus obtained than in the "high resistance system" for equal differences of tem-

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perature—the moving power for the indicating arm being approximately 150 times that actuating the delicately suspended needle of a galvanometer. A commercial pivot type of indicating instrument, such as a Weston milliameter with jewel bearings, may therefore be used in place of a delicate galvanometer.

The resistance is chiefly located at the indicating instrument, as in the high-resistance system, and may be provided with a mercury compensating device which is adapted to cut out resistance from the circuit in the same ratio as it is introduced through rise of temperature, and *vice versa*. Compensators may also be introduced along the leads if required.

The couples are composed of cheap alloys and are not the standard platinum and platinum-rhodium elements, although these may be used for extremely high temperatures. Owing to the comparative inexpensiveness of the materials used, the elements may be made of considerable cross-section and therefore be of extremely low resistance and any temperature effect thereon made inappreciable. The leads of ordinary copper wire are also of sufficient cross-section to render temperature effects thereon inappreciable.

It is difficult to compensate a high resistance instrument, because of the considerable amount of resistance it is necessary to vary to cause the correction.

The compensating device comprises a mercury thermometer, in the shank of which is a loop of fine platinum wire, adapted to be short-circuited, or *vice versa*, by the mercury.

To correct the cold-end-temperature error, a similar compensating device is inserted in series in the circuit and located in close proximity to the cold-end of the thermo-electric couple so as to be exposed to the same temperature as said cold end.

As the temperature of the cold end rises or falls, the electromotive force produced by the couple will be correspondingly decreased or increased for constant temperature at the hot end. It will now be readily understood that if the compensating device be properly constructed, the increase or decrease of temperature will cut out or insert resistance in the compensating device and therefore in the system in the correct amount to increase or cut down the electromotive force of the couple, thereby automatically maintaining the current constant for a given tem-

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perature at the hot end, irrespective of variations of temperature at the cold end.

This compensation is theoretically perfect for only one predetermined temperature of the hot end. In practice, however, a compensator serves to compensate sufficiently over a "working range," and approximately for a considerable part of the entire scale. In many instances, it is necessary to know only one particular temperature accurately.

It is also not practicable to apply a compensating device in this manner to the cold end of a thermo-electric couple of the high resistance system.

Another error is stated to be that the galvanometer needle sticks. This is not likely to occur in the low-resistance system, owing to the greater motive power behind the needle.

It is also stated that no extremely accurate readings may be obtained, owing to the closeness of the divisions of the scale—20° per millimeter. In the low-resistance type, with sufficient couples in series and with a large station milliameter, it is possible to read to a fraction of a degree. In one of the lower range scales (600° F.) each division corresponds to 10° F. and is about ⅛-inch long, so that one may readily estimate to one degree, Fahrenheit.

It is also stated that the couple must be placed in intimate contact with the material which is being investigated; and that the temperature at different parts of the furnace is not usually the same, and therefore the correct temperature is not generally obtained. These are purely mechanical difficulties, and the latter trouble may be remedied by placing a number of couples at various parts of a furnace, or the like, connecting them to a common indicating instrument, and, by means of a suitable switching device, the temperature of practically every point of the furnace may be quickly known.

Any lag error or slowness in reaching thermal equilibrium with object or inclosure, is to a great extent overcome by reducing the cross-section of the hot end of the couple, a practically instantaneous response to variations of temperature then being observed.

Mr. Shepherd has, through his paper, given the impression that the thermo-electric pyrometer is not quite a commercial, reliable, and accurate instrument, and is only suitable for those

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skilled in and familiar with the manipulation of delicate apparatus. In connection with explaining what has been done to correct some of the errors Mr. Shepherd has set forth, I have endeavored to remove this unfavorable impression, and wish to state that the thermo-electric pyrometer may be made a thoroughly commercial, accurate, and reliable instrument, able to withstand ordinary wear and tear, and capable of being entrusted to a workman of ordinary intelligence.

MR. BLOUGH: I would like to ask a question, in regard to the resistance of the circuit. I believe it was stated that the entire circuit had a low resistance. Suppose there is a small counter-electromotive force set up in some part of the circuit, what effect will that have on the percentage error of the instrument? I should think a counter-electromotive force in a low resistance instrument would cause a larger percentage error than in a high resistance galvanometer.

MR. SCHUETZ: I should think the percentage error would remain the same. As a matter of fact, the couples used in the lower resistance system generate more than 5 times the E. M. F. of the platinum-rhodium couple, and therefore the error is reduced in the ratio of 1 to 5.

MR. E. A. SPERRY: Recently I have taken a series of tests with the new instrument and there is most remarkable agreement with an accurate high reading thermometer throughout the range of the latter; when the couple is enclosed in an iron case one has to be careful about waiting until the temperatures are equalized; there is quite a marked lag; but if you have time enough (that is, three-fourths of a minute), you find that the agreement is most remarkable. I look upon the new pyrometer as one of great accuracy up to the point of, say, 1100°C.

MR. ALFRED COWLES: I am not sure of the make of the pyrometer that we use at Lockport; but we have had the same experience Mr. Sperry has; we can use it very easily up to about 1100°C. and watch it and get very close results.

MR. BURGESS: I have used two of these instruments in my laboratory work and found that they were satisfactory in some ways. They have the advantage of being cheap, convenient, easily made, and accurate if not subjected to too severe conditions. As being marketed at present we are not told whether the couple

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is of nickel-copper, of nickel-iron, of manganese-nickel. And the manufacturers simply tell us that there are a number of metals which can be used. That does not satisfy our curiosity; and, further, it does not give us a means of checking up the results if anything goes wrong. I wish to know in measuring a temperature much above 1,000°, whether there is any iron in the couple; if there is, I would not want to use it in any combination where there is carborundum; because my observations show that iron becomes very brittle when in contact with carborundum; a knowledge of the metals constituting the couples will enable us to guard against exposing them to harmful conditions. The Bristol pyrometers which I have used have given some trouble by becoming very brittle and breaking under careless treatment, and I have been inclined to trace this brittleness to the carborundum protective coating which is used for insulation.

PRESIDENT BANCROFT: Do I understand that the company declines to give information as to the composition of the couples they sell? If so, I should think that is a very distinct disadvantage.

MR. SCHUETZ: I cannot definitely answer that question. The couple is divided into two parts, the part which is in actual service termed the "Fire-End" being made replaceable so that a number of these parts may be ordered and be of the same composition. For the same range instruments the composition of the couples is uniform.

PROF. W. L. MILLER: The society might buy one and analyze it.

PRESIDENT BANCROFT: You don't know that the next one would be the same.

MR. HENRY HOWARD: I would like to ask if any one present has had any experience with the type of pyrometer which I saw in use at the blast furnace plant of the Lackawanna Steel Company. This apparatus is based upon the variation in the rate of flow of air of different temperatures through holes of a given size. I have never seen a diagram of the apparatus, but as explained to me, the hot air enters the apparatus through a small orifice in the end of a small tube which is placed in, and has the temperature of, the hot gases; the air is then cooled and passes out of the apparatus by a second orifice of the same size as the

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first, the current being produced by a constant suction applied beyond the second orifice. Owing to the increase in the density of the air as it cools, a greater weight passes through the second orifice, than through the first, under a given suction, with the result that a partial vacuum is produced in the tube between the two orifices. This vacuum varies with the temperature of the first orifice and is made to register by means of a column of colored water in front of a scale so made as to read directly in degrees centigrade.

DR. J. W. RICHARDS: That pyrometer is known as the Uhling pyrometer and is in considerable use in measuring the temperature of the blast for blast furnaces; but it is one of the most expensive pyrometers that there is on the market. I believe he charges something like $600, for one pyrometer. Its indications are said to be quite satisfactory.

I would like to also bear witness to the point brought up in the paper as to the importance of the time factor in measuring the reactions, and particularly of the disadvantage of measuring the temperature of reaction or formation of slags by putting them in the shape of a Seger cone. The temperature at which a slag will form from constituents which you mold in the shape of a Seger cone, depends very greatly on the fineness of the constituents before they are pressed together into the cone. Errors of two or three hundred degrees—or variations, I had better call them, of two or three hundred degrees in the temperature of formation of the slags and in their apparent melting point, may be obtained by differences in the fineness or coarseness of the constituents of the cones. A very long series of researches on blast furnace slags was made by Mr. Boudonard, an assistant of Le Chatelier, and reported to the Iron and Steel Institute, in which he used that method of determining the melting points by putting the substances in the shape of Seger cones; and we are certain that some of his results are as far as 250° out; so that possibly the whole investigation has been made worthless by neglecting this principle.

(Communicated after Adjournment.)

MR. E. S. SHEPHERD: If Mr. Schuetz's comment is intended for a discussion of the preceding paper, it

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has been written under a misapprehension. The paper was prepared for the purpose of calling the attention of the investigators who are at work on industrial problems to the fact that certain instruments are not suited for exact measurements except under fixed and definite conditions, and as a protest against their indiscriminate use in questionable situations. No objection was raised in the paper to the use of any kind of instrument whatsoever for routine commercial work.

The merits of Mr. Schuetz's instrument cannot yet be very satisfactorily discussed because he gives no figures whatever. When he says that "*much better* results are obtained using cheaper elements composed of nickel, steel, tungsten, copper, constantan, nickel steel, German silver, etc.," it is a little hard to know just what he means by "much better." If he means that elements made of these materials give perfectly concordant results of long periods of time, it is very important that he bring forward data to this effect. For most scientific investigation an element which is not constant to a fraction of a degree is untrustworthy, and the experience with these alloys which has already been recorded is so universally to the effect that constant results cannot be expected of them (due to various causes, including especially oxidation), that there must be some hesitation in accepting this sweeping statement unsupported. Until it can be shown that certain well defined fixed temperatures can be repeatedly and correctly measured, even after a considerable lapse of time, with Mr. Schuetz's instruments, we are not in a position to say how completely the various correcting devices fulfill their functions. While it is interesting to note that 10° F. of the scale on the instrument, going up to 350° C. is an eighth of an inch long, this in itself suggests no special advantage in accuracy over a good mercury thermometer. It is after all not so important that the scale have broad divisions as that when the instrument indicates a given temperature, the element (and the substance being investigated) is really at that temperature, and that the results of successive observations will agree.

In what has been said above, I have in mind only the possible usefulness of the instrument for purposes of scientific investigation of industrial problems. Whatever its value as a commercial instrument may be, no data have yet been presented to show that it is free from the errors whch were discussed in the paper.

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(Communicated after Adjournment.)

MR. CARL HERING: In this connection, I might again call attention to a simple method of measuring high temperatures, which, though not a true scale method, may have advantages in particular cases. It is somewhat analogous to the well-known scale of hardness used by mineralogists; it is not a new idea, but has perhaps not received the attention which it may deserve.

It consists in selecting from almost innumerable available substances, a series which will melt, volatilize, or change in some other visible way, at a series of fixed temperatures over the ranges desired. The temperature at which these changes take place can be accurately predetermined in the laboratory, and the introducing of a small quantity of one of these materials in the furnace will then serve to determine whether the temperature in the furnace has reached that particular point or not. Two or more of them selected for different temperatures would show that the temperature was between two of these known values. By making the number of materials sufficiently great, the ranges between any two might be made relatively small. If made in the form of powder or fine crystals, the fact that they had been melted would become easily visible. In some cases, several substances might be mixed together as powders, and when afterwards examined, would show which of them had fused, thereby indicating the temperature. If they are in powdered form, they might be placed in small infusible tubes which are inserted in the furnace.

This method, of course, is not intended to do all that an indicating thermometer or pyrometer would do, and would at best be limited in its application. But, as the characteristic temperatures of the materials can be predetermined very accurately in the laboratory, it seems to me it might give very accurate and reliable results in such cases in which it could be used, especially as in many cases the important point to know is, whether a certain fixed temperature has been reached, or whether it has been exceeded; to know that accurately and reliably, may often be more important than to know how much greater or less the temperature was.

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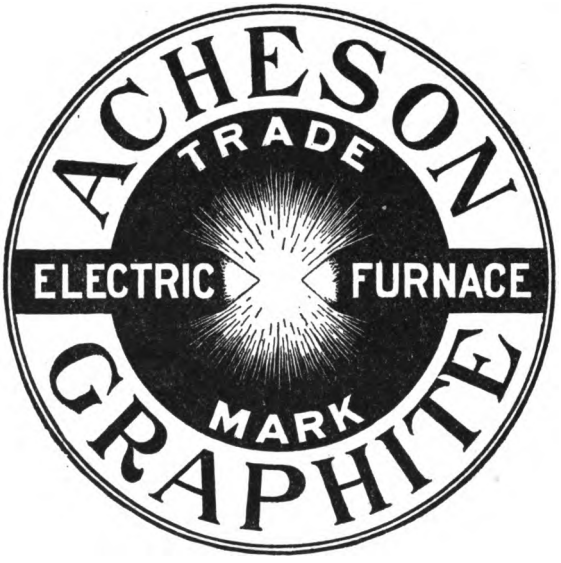

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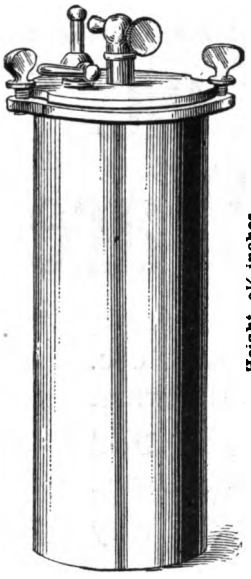

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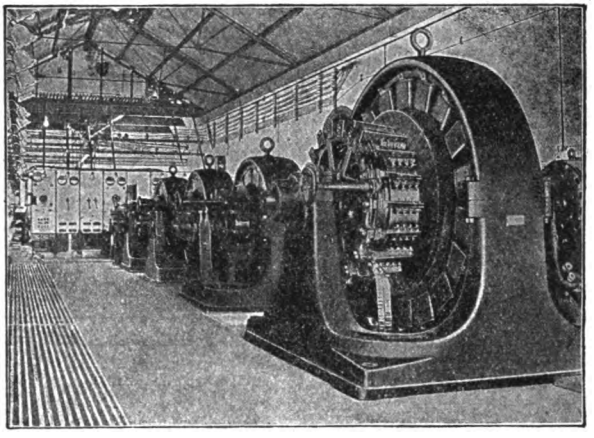

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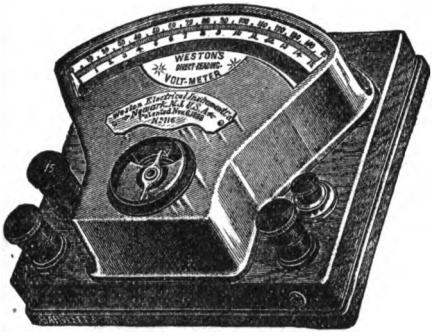

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